Technetium-99 (^{99}Tc) in the North and Nordic Seas

– the present status (2010) and a compilation of the Institute of Marine Research's monitoring data (2003-2009)

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Preface

This master project has been a collaboration between the University of Bergen and the Institute of Marine Research (IMR). The laboratory work was performed at the Chemistry Laboratory at the Institute of Marine Research.

First of all, I would like to thank my supervisors, Dr. Hilde Elise Heldal at IMR and Professor Leif J. Sæthre at the Department of Chemistry, UiB for giving me an interesting project and for excellent supervision throughout the master project. Thank you, Hilde Elise for always having time for me, your good advices and comments!

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Hilde Marie Mjøs Karlsen

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List of abbreviations

AW	Atlantic Water
BLK	blank
BNFL	British Nuclear Fuels Limited
Bq	Becquerel
CEFAS	Centre for Environment, Fisheries & Aquaculture Science
CF	Concentration factor
cps	counts per second
CTD	Conductivity, Temperature, Depth
dps	disintegrations per second
d.w.	Dry weight
EARP	Enhanced Actinide Removal Plant
EGC	East Greenland Current
FIC	Fair Isle Current
IAEA	International Atomic Energy Agency
ICRP	International Commission on Radiological Protection
IFE	Institute for Energy Technology
IMR	Institute of Marine Research
K_d	Distribution coefficient
MAC	Medium Active Concentrate
MARiS	Marine Information System
NAC	North Atlantic Current
NRPA	Norwegian Radiation Protection Authority
NwAC	Norwegian Atlantic Current
NwCC	Norwegian Coastal Current
OSPAR	the (Oslo-Paris) Convention for the Protection of the marine Environment of the North-East Atlantic
PBq	Peta becquerel (10^{15})
pers. comm.	Personal communication
psu	practical salinity unit
QC	Quality control
RAME	Radioactivity in the Marine Environment

RIFE	Radioactivity in Food and the Environment
ROMS	Regional Ocean Modeling System
R/V	Research Vessel
SCC	Scottish Coastal Current
SD	Standard deviation
$T_{1/2}$	Half-life
^{99}Tc	Technetium-99
TBq	Tera becquerel (10^{12})
TF	Transfer factor
TPP	Tetraphenylphosphonium bromide
w.w.	Wet weight
WSC	West Spitsbergen Current

SI prefixes

Factor	**Prefix**	**Symbol**
10^{-3}	milli	m
10^{3}	kilo	k
10^{6}	mega	M
10^{9}	giga	G
10^{12}	tera	T
10^{15}	peta	P

Abstract

Technetium-99 (^{99}Tc) is an anthropogenic, pure β-emitting (E_{max} = 292 keV) radionuclide with a half-life of $2.13 \cdot 10^5$ years. It is present in the marine environment primarily due to discharges from nuclear fuel reprocessing facilities and global fallout from nuclear weapons testing during the 1950s and 1960s. During the period 1994-2004, large amounts of ^{99}Tc were discharged into the Irish Sea from the nuclear reprocessing plant Sellafield (UK). Technetium-99 (as the highly soluble pertechnetate ion, TcO_4^-), is transported by ocean currents from the Irish Sea to the North Sea and Skagerrak, and further northwards to the Norwegian and Barents Seas via the Norwegian Coastal Current (NwCC).

In July/August 2010, 20 surface seawater samples from the North Sea, Skagerrak and the NwCC were collected during a cruise aboard R/V *Johan Hjort*. The first radiochemical separation step (addition of rhenium (Re) as yield monitor and preliminary anion-exchange) was performed aboard the ship. The subsequent radiochemical analyses were carried out at the Chemistry Laboratory of the Institute of Marine Research (IMR). The analytical method is based upon Harvey et al. (1992). After iron hydroxide scavenging, ^{99}Tc and Re were further extracted by a second anion-exchange separation and subsequent sulphide precipitations. Finally, their tetraphenyl arsonium salts were isolated. The yield of the rhenium tetraphenyl arsonium salt was determined gravimetrically, and ^{99}Tc was beta-counted using a RISØ low-level beta-counter. The ^{99}Tc activity concentrations ranged from 0.12±0.01 to 0.77±0.04 Bq m^{-3}, with a mean value of 0.33±0.14 Bq m^{-3}. The maximum ^{99}Tc activity concentration was measured in a sample collected off the east coast of Scotland. The ^{99}Tc level in the NwCC (mean activity concentration 0.34 Bq m^{-3}) was a factor of 2 lower than the concentration observed off the Scottish coast. The lowest activity concentrations were found in samples from the north-western part of the North Sea with high influence of inflowing high salinity, radionuclide poor Atlantic water.

A compilation of IMR's historical monitoring data (2003-2009) on ^{99}Tc in the North and Nordic Seas was performed in order to investigate trends. Data from an IMR/CEFAS (Centre for Environment, Fisheries and Aquaculture Science) study (1998-2000) was also included. Overall, the results show that the ^{99}Tc activity concentrations in the North and Nordic Seas are generally decreasing following the reduction in the discharges from Sellafield.

1. Introduction

1.1 Background

The British nuclear fuel reprocessing plant Sellafield, located on the west coast of Cumbria (UK), has received much attention in Norway because of the discharges of radioactive substances to the marine environment. Between 1994 and 2004, Sellafield discharged large amounts of technetium-99 (^{99}Tc) into the Irish Sea (e.g. (Leonard et al., 1997, Kershaw et al., 1999, McCubbin et al., 2002, Kershaw et al., 2004) causing socio-political concerns particularly in countries like Norway and Ireland.

As a consequence of the increased discharges of ^{99}Tc from Sellafield, elevated activity concentrations in seawater and marine organisms were observed at the end of the 1990s and early 2000s. Although the levels of ^{99}Tc detected did not represent any known health hazard, the discharges caused concerns in the Norwegian fisheries and seafood industries. Radioactive contamination, or any rumours of such contamination, may have a negative impact on the markets for Norwegian seafood.

The discharge of ^{99}Tc from Sellafield has been considerably reduced since 2004. Today a decrease in the activity concentrations in the marine environment is observed, and a further reduction is expected to be observed in the years to come.

In spite of the negative impacts mentioned above, the elevated ^{99}Tc discharges became a renewed time-dependent oceanographic tracer for studying the circulation of the North-East Atlantic and the North and Nordic Seas from the mid-1990s and onwards (e.g.(Orre et al., 2007, Kershaw et al., 2004). The controlled discharges of ^{99}Tc from European reprocessing plants have been used earlier as an oceanographic tracer in many studies of long distance transport of radioactive contamination from Europe to the Arctic (e.g. Aarkrog et al., 1986, Aarkrog et al., 1987, Kershaw et al., 1999). Measurements of ^{99}Tc in the marine environment, and particular in seawater, serve as a valuable tool in the validation of hydrodynamic models that can be used to simulate Sellafield release scenarios. Such models are of crucial importance in order to predict the environmental and radiological consequences of radioactive contamination to the North and Nordic Seas following a hypothetical accident at Sellafield.

1.1.1 Objective of the study

The objective of this study was threefold:

1. To investigate the activity concentrations of ^{99}Tc in the North Sea and Skagerrak in July 2010.
2. To compile the Institute of Marine Research's (IMR) historical monitoring data on ^{99}Tc in seawater. The purpose with this compilation is to investigate trends and document the decrease in activity concentrations of ^{99}Tc after the reduction in the discharges from Sellafield.
3. To provide a dataset of ^{99}Tc activity concentrations that can be used for comparisons with results from the 3D numerical ocean model ROMS (Regional Ocean Modeling System) used by oceanographers at IMR. This comparison was planned to be done within the frame of this master project. Unfortunately, the latter proved not to be possible within the available time frame.

The spatial and temporal distribution of ^{99}Tc in the North and Nordic Seas is discussed in relation to historical discharge data from Sellafield and available hydrographical data (temperature and salinity). The IMR data is also compared with available literature data, and transit times and transfer factors of ^{99}Tc from Sellafield to Norwegian waters are discussed.

1.2 About Technetium

1.2.1 The discovery of technetium and its position in the periodic table of elements

Element 43 in the periodic table was discovered by Perrier and Segré in 1937, by bombarding molybdenum with deuterons (Perrier and Segré, 1937). They called the element technetium, derived from the Greek word *technetos* meaning artificial, since it was the first artificially produced element (Perrier and Segré, 1947).

Figure 1.1 shows the position of technetium (Tc) in the periodic table of elements. Technetium is member of group 7A in the periodic table and belongs to the transition metals. It is placed between manganese (Mn) and rhenium (Re), but its chemical properties most closely resemble those of rhenium (Harvey et al., 1991). The elements of group 7 have seven s + d electrons and the electron configuration of technetium is [Kr]$4d^5 5s^2$.

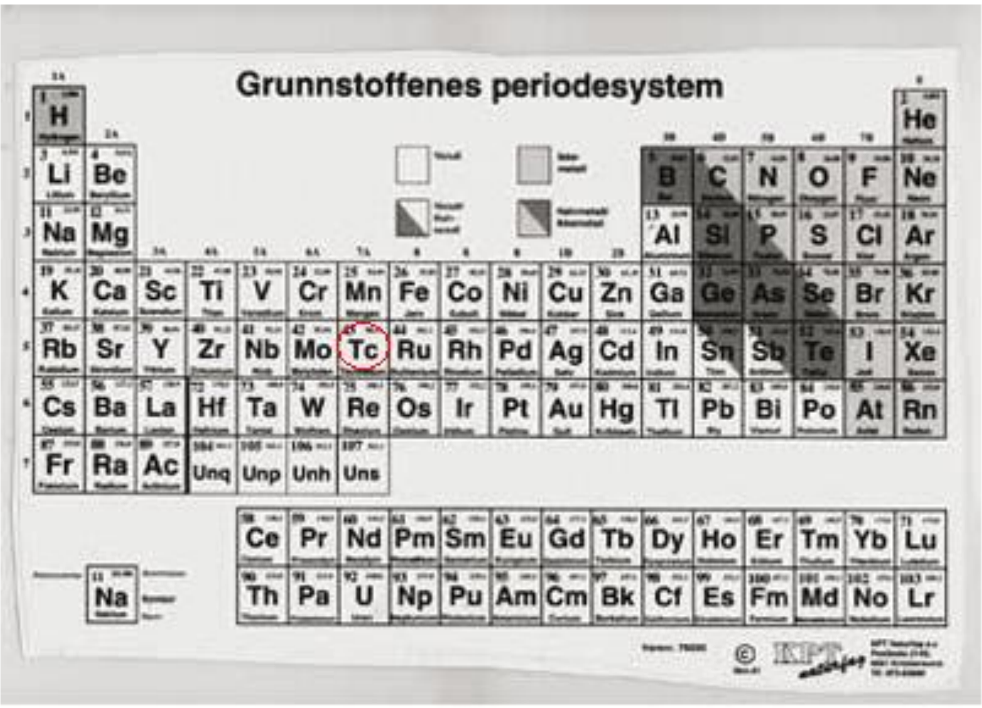

Figure 1.1: The element technetium (Tc) with atomic number 43 in the periodic table of the elements. (Source: http://www.mamut.net/homepages/Norway/1/18/kometnaturfag/102232.jpg)

1.2.2 Chemical and physical properties

Technetium is the lightest element with no stable isotopes, and 21 radioactive isotopes and 7 isomers are known. The most stable isotopes are ^{98}Tc ($t_{1/2}$ =4.2 · 10^6 years), ^{97}Tc ($t_{1/2}$ = 2.6 · 10^6 years) and ^{99}Tc ($t_{1/2}$ = 2.1 · 10^5 years). Because of its long half-life and relatively high fission yield (approximately 6 %), ^{99}Tc is the only technetium isotope of radiological importance (Salbu and Holm, 2005).

Technetium-99 is the daughter nuclide of molybdenum-99 (^{99}Mo), which is produced by thermal neutron fission of uranium-235 (^{235}U) or plutonium-239 (^{239}Pu) or by neutron activation of ^{98}Mo (e.g. NRPA, 2009). ^{99}Tc is a pure β-emitting radionuclide with maximum β – particle energy (E_{max}) of 292 keV (e.g.(Aarkrog et al., 1987), and has a specific activity of 636 ·10^6 Bq/g. The decay scheme for ^{99}Mo is shown in figure 1.2. The mother nuclide ^{99}Mo disintegrates by beta decay to the metastable isotope ^{99m}Tc, which has a half life of only 6.02 hours (e.g. Salbu and Holm, 2005), and decays by gamma emission to ^{99}Tc. ^{99}Tc disintegrates by expelling a low-level energy β – particle, to the stable nuclide ruthenium-99 (^{99}Ru):

$$^{99}Mo \xrightarrow{(\beta^-,\gamma,67\,h)} {}^{99m}Tc \xrightarrow{(\gamma,6,02\,h)} {}^{99}Tc \xrightarrow{(\beta^-,2.11\cdot 10^5\,y)} {}^{99}Ru(stable)$$

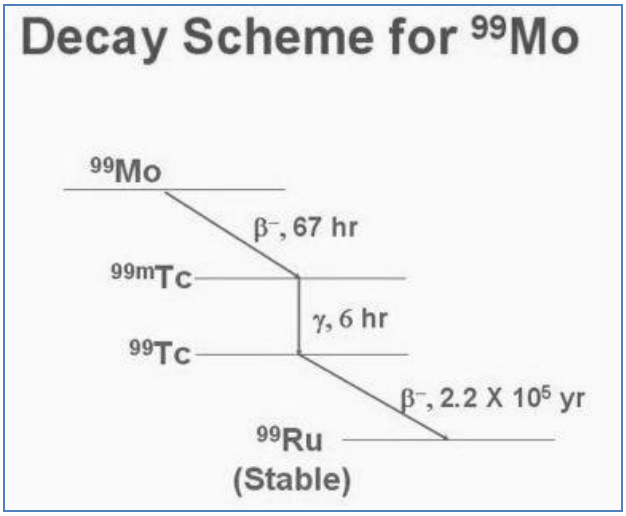

Figure 1.2: Decay scheme for ^{99}Mo. (Source: http://www.nucmedconsultants.com/tutorials/gen2008/genealogy.htm)

Technetium can exist in a large number of oxidation states, but the most stable compounds are heptavalent (VII), and to a lesser extent, tetravalent (IV). When Tc is heated in air, the heptaoxide Tc_2O_7 is produced ($4Tc_{(s)} + 7O_{2\,(g)} \rightarrow 2Tc_2O_{7(s)}$). When this oxide is dissolved in water it gives an acidic solution of pertechnetate, TcO_4^- (Kofstad, 1992).

The physicochemical form of technetium in aqueous solution is dependent on pH and redox conditions. From the Pourbaix-diagram (E_h[1]- pH-diagram) of technetium in figure 1.3, it can be seen that under aerobic conditions, TcO_4^- is the only stable specie of technetium in seawater (pH~8), thus it can be concluded that in oxygenated seawater, ^{99}Tc will be present as TcO_4^- (Beasley and Lorz, 1986). Due to the fact that the pertechnetate anion has a low affinity to adsorb on particulate matter, with distribution coefficients (K_d = sediment activity concentration, Bq kg^{-1} / seawater activity concentration, Bq L^{-1}) rarely exceeding 1-4 for sediments low in organic matter (Beasley and Lorz, 1986), ^{99}Tc is considered as a conservatively (i.e. soluble) radionuclide. (As opposed to for example plutonium-239+240 (^{239}Pu + ^{240}Pu) and americium-241 (^{241}Am) which are generally considered as particle reactive or non-conservative radionuclides, with k_d's=$1 \cdot 10^5$ and $2 \cdot 10^6$, respectively (IAEA, 2004)). However, under reducing (anaerobic) conditions, TcO_4^- will be reduced to TcO_2(s) or intermediate species such as $TcO(OH)_2$ and $TcCl_6^{2-}$ (Beasley and Lorz, 1986, Salbu and Holm, 2005). These species with technetium in oxidation state IV are particle reactive and will be retained in sediments. Thus, under reducing conditions and/or interacting with sediments high in organic matter, technetium will behave less conservatively. K_d-values for technetium in sediments high in organic matter can be notably high. For example, McCubbin et al. (2006) reported an average environmental K_d – value of $1.9 \cdot 10^3$ for ^{99}Tc in the Irish Sea. In liquid effluents from nuclear reprocessing plants, technetium is assumed to be released as the highly soluble and mobile pertechnetate ion, TcO_4^- (Leonard et al., 1995).

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[1] E_h is the E° (standard reduction potential) value recalculated for pH 7

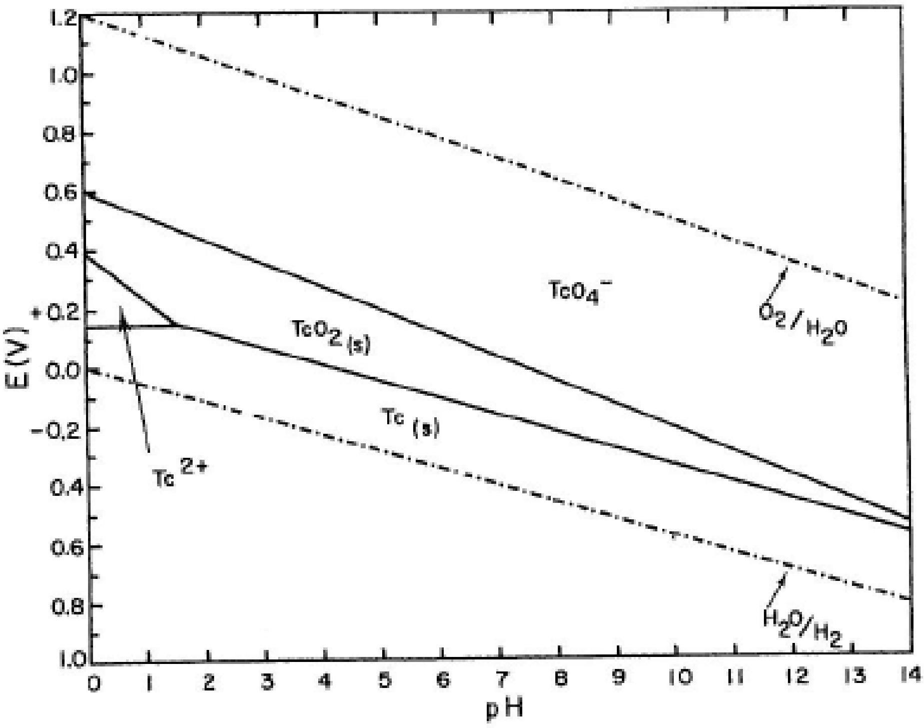

FIG. 1. Stability diagram of the various chemical forms of Tc under different environmental conditions of E_h and pH. For well-oxygenated seawater, $E_h = 0{\cdot}4$ V and pH = 8; predicted form of Tc under these conditions is TcO_4^-.

Figure 1.3: E_h-pH diagram of technetium. In oxygenated seawater where E_h=0.4 and pH=8, the most stable for of Tc is TcO_4^-. From Beasley and Lorz (1986).

1.3 Sources of ^{99}Tc to the marine environment

The two main sources of ^{99}Tc to Northern European waters are discharges from the European nuclear reprocessing plants Sellafield (UK) and Cap de La Hague (France). These nuclear fuel reprocessing plants enables recycling of spent fuel (uranium and plutonium) for reuse in fission reactors (for more information about the nuclear fuel cycle, see Appendix 1). The remaining waste, containing fission products, is either sent to final storage or discharged to the environment. In addition to the authorized discharges from Sellafield and La Hague, global fallout from nuclear weapons testing during the 1950s and 1960s has also been a source for ^{99}Tc to the marine environment.

1.3.1 Discharges of ^{99}Tc from Sellafield – a historical context

The reprocessing plant Sellafield (formerly Windscale) has performed controlled discharges of low-level liquid effluents via pipelines directly into the Irish Sea since 1952, and has been the main contributor of discharged radioactivity among the European nuclear fuel reprocessing plants (Kershaw and Baxter, 1995). The discharges of most radionuclides from

Sellafield peaked in the mid- to late-seventies, and releases have been reduced during recent years. The releases are well documented; annually discharges have been reported through BNFL reports (1978-1995; Leonard et al. (1997) and Radioactivity in Food and the Environment (RIFE) reports (RIFE-1, 1996, RIFE-2, 1997, RIFE-3, 1998, RIFE-4, 1999, RIFE-5, 2000, RIFE-6, 2001, RIFE-7, 2002, RIFE-8, 2003, RIFE-9, 2004, RIFE-10, 2005, RIFE-11, 2006, RIFE-12, 2007, RIFE-13, 2008, RIFE-14, 2009, RIFE-15, 2010). Annual discharges of technetium-99 from Sellafield and La Hague during the period 1952 – 2009 are presented in figure 1.4. The annual Sellafield discharge data of technetium prior to 1978 are estimated values based upon measurements of brown seaweed using data from Särdal, a sampling location in Sweden and from sampling sites in the Arctic during the period 1965-1982 (Aarkrog et al., 1987, Aarkrog et al., 1986).

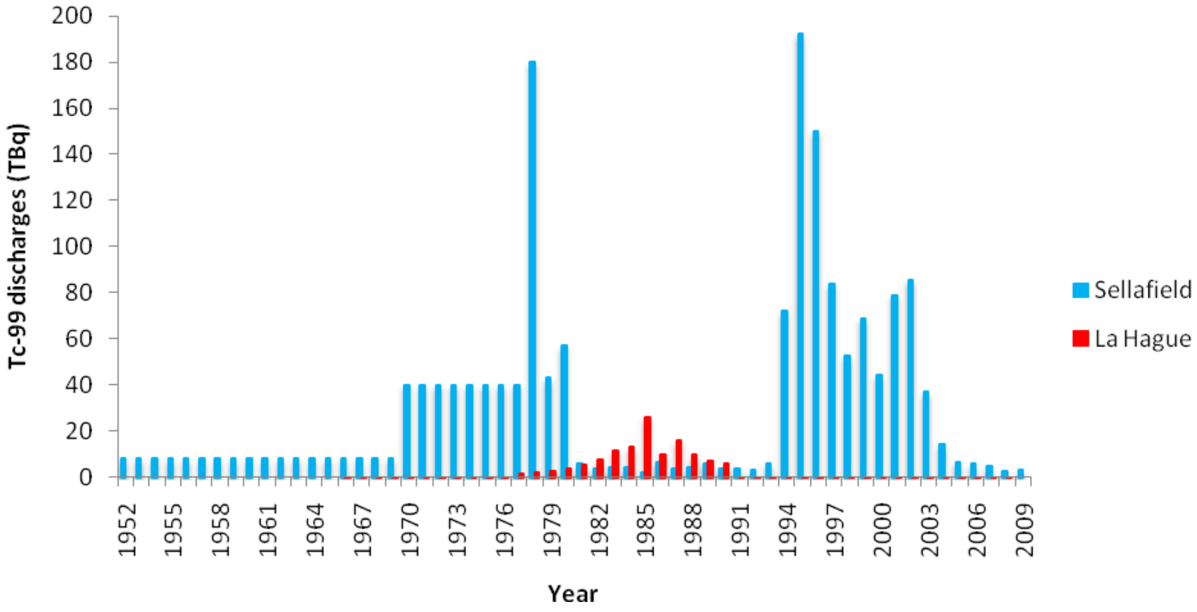

Figure 1.4: Annual discharges of ^{99}Tc from Sellafield (blue) and La Hague (red) in the period 1952-2009.

Annually, approximately 30 TBq of ^{99}Tc from the reprocessing of spent nuclear Magnox fuel (see Appendix 1) is produced at the Sellafield site (Amundsen et al., 2003). Approximately 770 TBq was discharged into the Irish Sea in the period 1952 – 1994, with a reported maximum annual release of 178 TBq in 1978 (e.g. Salbu and Holm, 2005). During the period from 1981 to 1994, medium-level waste was stored in containers at the site awaiting the commission of the treatment plant EARP (Enhanced Actinide Removal Plant), which became operational in April 1994. It was designed to treat the stored waste, and the treatment, based on ultrafiltration of precipitated ferric hydroxide flocs, removed a range of radionuclides (e.g. ^{106}Ru and actinides like plutonium and americium) from the effluents, but it did not remove technetium (Hunt et al., 1998, Lindahl et al., 2003). Before EARP began operation, it was well known that the EARP method would not remove ^{99}Tc from the waste. However, this was not considered important enough to adopt a more expensive and advanced treatment method (Amundsen et al., 2003). Consequently, the discharges of ^{99}Tc increased significantly, from a level of 2-7 TBq/year during the 1980s and early 1990s (e.g. Brown et al., 1999), to a peak level of 192 TBq/year in 1995. The monthly discharge data in figure 1.5 shows the pulsed nature of the elevated ^{99}Tc discharges following the operation of EARP. In 2000 the discharge limit was reduced from 200 TBq/year to 90 TBq/year due to high concentrations of ^{99}Tc in biota in the Irish Sea (e.g. Salbu and Holm, 2005). British Nuclear Fuels Plc (BNFL), a company owned by the UK Government, was the owner and operator of the Sellafield site at that time. British authorities intended to continue the discharges of ^{99}Tc at a high level up until 2006, with a discharge limit of 90 TBq/year, and then reduce the limit to 10 TBq/year (Amundsen et al., 2003). However, they were forced to change their plans.

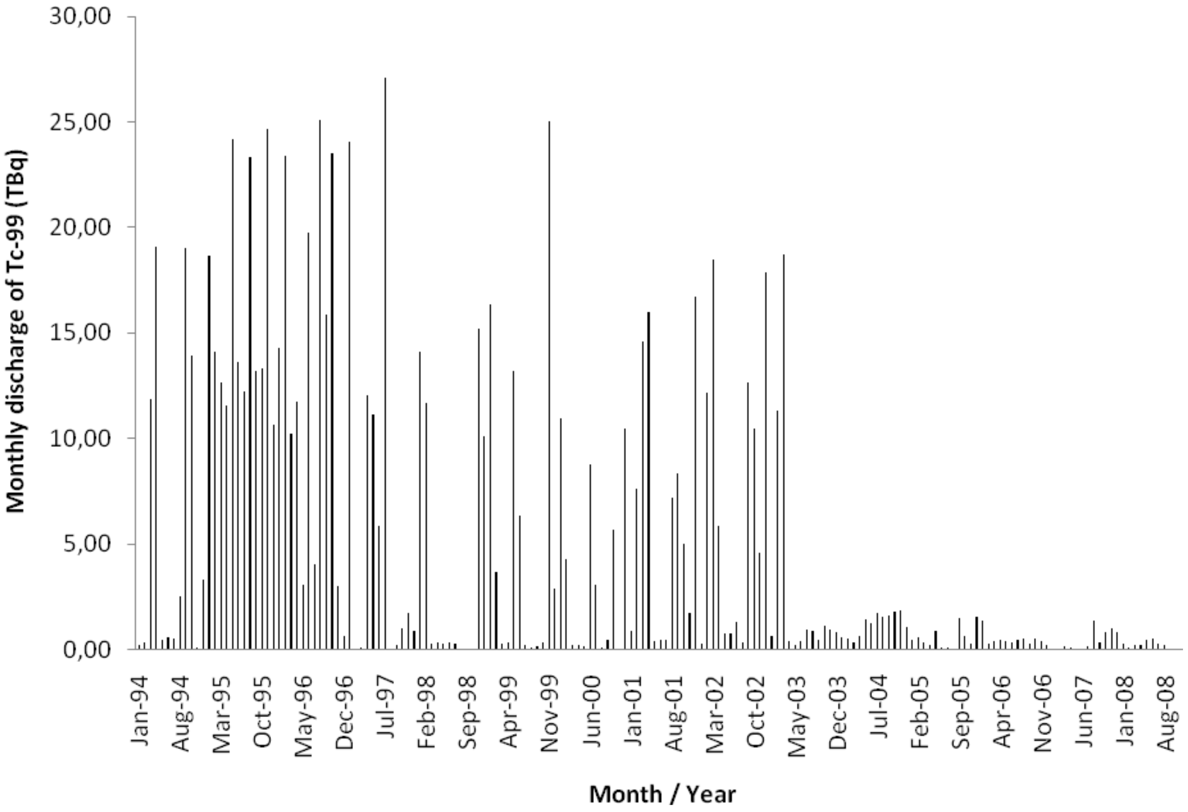

Figure 1.5: Monthly discharges of ^{99}Tc from Sellafield in the period 1994-2008 (Sellafield Ltd. (data provided by Justin Gwynn via Hilde Elise Heldal)).

Because ^{99}Tc is a conservatively behaving radionuclide, it is transported with ocean currents to Norwegian waters. In 1996, two years after EARP began operation, the Norwegian Radiation Protection Authority measured elevated levels of ^{99}Tc in seawater, seaweed and lobster along the Norwegian coast (Brown et al., 1998, Brown et al., 1999).

This received public concern in Norway during the late 1990s and early 2000s. Strong criticism and protests against Sellafield were communicated from the Norwegian Government, media, environmental organizations (e.g. Bellona) and local community groups (e.g. 'Lofoten mot Sellafield')(Osborne and Huston, 2009, Regjeringen.no, 2002). The goal of the Norwegian stakeholders was to stop the discharges from Sellafield. The Norwegian Government co-operated with the governments of the other Nordic countries and Ireland in order to put pressure on the British authorities.

An important forum for international co-operation on reducing radioactive discharges to the marine environment is within the framework of the OSPAR Convention (The Convention for the Protection of the marine Environment of the North-East Atlantic). The member countries of the OSPAR commission (among them the United Kingdom) had through the "Sintra declaration" from the 1998 OSPAR Ministerial Meeting committed themselves to prevent radioactive contamination of the Seas making *"progressive and substantial reductions in discharges, emissions and losses of radioactive substances, with the ultimate aim of concentrations in the environment near background values for naturally occurring substances and close to zero for artificial radioactive substances"* (quoted in Amundsen et al., 2003:17). Referring to the commitment the UK had given in the Sintra declaration both the Irish and Norwegian Government were putting considerably political pressure on the British Government in order to stop the discharges of technetium-99. The Environment Minister of Norway at that time, Børge Brende, had several meetings with his colleagues in the UK regarding the Sellafield case.

In 2003, after pressure from the Norwegian Government (Osborne and Huston, 2009), the British authorities finally introduced a moratorium on discharges in order to investigate the use of a new treatment process using tetraphenylphosphonium bromide (TPP) (StrålevernInfo, 2004). Discharges of ^{99}Tc were reduced as newly created Medium Active Concentrate (MAC) waste from the Magnox fuel reprocessing plant was re-routed to the vitrification plant instead of being treated at the EARP plant (RIFE-9, 2004, Smith et al., 2009). During the process of vitrification, the liquid waste is being converted into a glasslike substance that can be stored in steel tanks (Martiniussen, 2003). In October-November 2003, BNFL carried out a trial use of TPP in EARP in order to remove ^{99}Tc from the already stored MAC that was chemically unsuitable for vitrification. In the TPP-treatment process, TPP is added to the liquid waste, precipitating technetium and other substances, and then the precipitated waste is encapsulated in concrete and stored on land. The trial use of TPP was very successful, and in 2004 this new treatment for removing ^{99}Tc from old MAC-waste, was implemented at EARP, causing a 90 % reduction in the discharges of ^{99}Tc (StrålevernInfo, 2004). The last untreated discharge of ^{99}Tc occurred during the spring 2003 (StrålevernInfo, 2004). As the transport time from the Irish Sea to the Norwegian coastal areas is about 3-4 years, the effect of the reduced discharges was therefore expected to be observed in Norwegian waters around 2007.

By the end of 2007, all of the remaining stored MAC waste at Sellafield had been treated, and the discharges from this main source of ^{99}Tc at Sellafield finally ceased (OSPAR, 2009b, OSPAR, 2010b). Hence, the current discharges of ^{99}Tc from the Sellafield site, resulting from present day activity, are reduced to pre-EARP levels (3.08 TBq in 2009 (RIFE-15, 2010)), and the discharge limit is 10 TBq/year. Sellafield Ltd is presently the company responsible for decommissioning, reprocessing, nuclear waste management and fuel manufacturing activities at the Sellafield site, on behalf of the Nuclear Decommissioning Authority (NDA) (Sellafield.Ltd, 2011).

In the period 1994-2004, 879 TBq (=1400 kg)[2] of ^{99}Tc was discharged from the Sellafield site into the Irish Sea, this corresponds to more than 50 % of the total amount of ^{99}Tc discharged in the period 1952-2009 (approximately 1703 TBq = 2700 kg). Table 1.1 presents the annual discharges of ^{99}Tc from Sellafield in the years 1990 to 2009 both in TBq per year and kg per year.

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[2] Converted into mass unit by the author. From the specific activity of ^{99}Tc ($636 \cdot 10^6$ Bq/g), we find that 1 TBq (10^{12}Bq) ^{99}Tc released corresponds to approximately 1.6 kg of ^{99}Tc [10^{12} Bq/($636 \cdot 10^6$ Bq/g)=1575 g].

Table 1.1: Annual discharges of ^{99}Tc from Sellafield (1990-2009) in TBq/year and kg/year. Converted into mass units by the author. The table is based on a table given in Nies et al. (2009). Discharge data 1990-2006: OSPAR-data in (Nies et al., 2009). Discharge data 2007-2009: RIFE-reports (RIFE-13, 2008, RIFE-14, 2009, RIFE-15, 2010).

Year	**1990**	**1991**	**1992**	**1993**	**1994**	**1995**	**1996**	**1997**	**1998**	**1999**
Discharge (TBq/a)	3.8	3.9	3.2	6.1	72	192	150	84	52.7	*68.8*
Discharge (kg/a)	6.08	6.24	5.12	9.76	115	307	240	134	84.3	110
Year	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**2008**	**2009**
Discharge (TBq/a)	*44.4*	*79*	*85.4*	*36.8*	*14.3*	*6.7*	*5.6*	*4.9*	*2.4*	*3.1*
Discharge (kg/a)	71.0	126	136.64	58.9	22.9	10.7	8.96	7.84	3.84	4.96

1.3.2 Discharges of ^{99}Tc from La Hague

The AREVA La Hague reprocessing plant, located on the Cotentin Peninsula in Normandy (France), began operation in 1966. The plant discharges radionuclides into the English Channel (Kershaw and Baxter, 1995). While Sellafield has been the main source of ^{137}Cs, ^{134}Cs, ^{90}Sr, ^{99}Tc and Pu-isotopes to the marine environment, La Hague has contributed a larger proportion of ^{129}I and ^{125}Sb (Kershaw and Baxter, 1995). From the discharge data given in figure 1.4 it is clear that Sellafield has been the main source of ^{99}Tc to the Northern European marine environment. However, in the period 1981 to 1990, the discharges from La Hague were greater than from Sellafield. In the period 1982 – 1993, a total of 102 TBq ^{99}Tc were discharged from La Hague (Herrmann et al., 1995), compared with 51 TBq discharged from Sellafield during the same period (BNFL 1982-1993, data provided by Justin Gwynn via Hilde Elise Heldal). The releases of ^{99}Tc from La Hague reached its maximum in 1985 (approximately 25 TBq/year), figure 1.4. However, during the late 1980s and 1990s the ^{99}Tc discharges from La Hague decreased significantly (Masson et al., 1995). In 1990 a specific removal process involving chemical extraction and vitrification was implemented at La Hague, and discharges of ^{99}Tc were reduced by a factor of 100 between 1989 (~7 TBq/year) and 2004 (~0.07 TBq/year) (OSPAR, 2009b). Today, less than 0.06% of the input of this radionuclide to the plant is being released to the marine environment (OSPAR, 2009b). The estimated discharges of ^{99}Tc from La Hague in the period 1966 – 2008 are approximately 130 TBq (data provided by Justin Gwynn via Hilde Elise Heldal; OSPAR-reports (OSPAR, 2008, OSPAR, 2009a, OSPAR, 2010a)). Information on discharges of ^{99}Tc from La Hague during recent years is available in OSPAR-reports (e.g. (OSPAR, 2008, OSPAR, 2009a, OSPAR, 2010a). In 2008, the annual release of ^{99}Tc from La Hague was 0.074 TBq/year (OSPAR, 2010a).

1.3.3 Global fallout from nuclear weapons testing

The total release of ^{99}Tc to the environment as a result of nuclear weapons testing between 1945 and 1963 is assumed to be approximately 180 – 200 TBq (Salbu and Holm, 2005). Dahlgaard et al. (1995) measured the fallout "background" concentration of ^{99}Tc in oceanic NE Atlantic surface waters as 0.005 Bq m^{-3}.

1.3.4 Other sources of ^{99}Tc to the marine environment

Natural background

Trace amounts of ^{99}Tc has been found in mineral ores as a result of spontaneous fission of naturally occurring ^{238}U (Kenna and Kuroda, 1964), but this is a negligible source. The natural background of ^{99}Tc due to spontaneous fission would give a seawater concentration of approximately 10^{-6} Bq m^{-3} (Dahlgaard et al., 1995).

Nuclear medicine

Another source of ^{99}Tc to the environment include disposal of ^{99m}Tc from the medicinal sector. The short-lived isotope ^{99m}Tc ($t_{1/2}$ = 6.02 h) is widely used in nuclear medicine for diagnostic purposes. Because technetium has the ability to be chemically bound onto many biologically active molecules, and ^{99m}Tc sends out gamma radiation, internal body organs can be imaged using gamma-scintigraphy (OSPAR, 2009b). According to OSPAR (2009), approximately 85% of the diagnostic imaging procedures in nuclear medicine today use this isotope. However, the amount of ^{99}Tc discharged to the environment from this source is negligible. The Norwegian Radiation Protection Authority (NRPA) estimated the total annual discharged activity of ^{99}Tc from the medical sector in Norway in 2007 as 0.06 MBq (NRPA, 2009). In 2009, the Radioactive Substance committee of the OSPAR commission concluded that they would cease to include reporting on ^{99}Tc from the medical sector because of the very small contribution (approximately 1 MBq/year in the OSPAR region) compared with discharges in the TBq range (i.e. several million times more) from nuclear fuel reprocessing plants (OSPAR, 2009b).

The Chernobyl accident

After the Chernobyl accident in 1986, Aarkrog et al. (1988) measured the levels of ^{99}Tc in the Kattegat and Baltic Sea, and found ^{99}Tc activity concentrations of 1-2 Bq m^{-3} in the Kattegat, while levels dropped below 0.1 Bq m^{-3} in the Baltic Sea. In comparison, ^{137}Cs activity concentrations in the range 20-960 Bq m^{-3} were measured in the Baltic Sea, and no correlation between radiocaesium and ^{99}Tc in the seawater samples was found. Aarkrog et al. (1988) therefore concluded that the Chernobyl accident did not cause elevated levels of ^{99}Tc in the Baltic Sea. The reported radionuclide ratio ^{99}Tc/^{137}Cs in the fallout from the Chernobyl accident was 1.5 x 10^{-5} (which is significantly lower than the theoretical estimate for fission, 1.43 x 10^{-4}) (Salbu and Holm, 2005).

Table 1.2 shows the amount of ^{99}Tc released from the most important sources to the marine environment.

Table 1.2: Sources of ^{99}Tc to the marine environment (1952-2009)

Source	**^{99}Tc (TBq)**	**References**
Sellafield	1703	(BNFL (data provided by Justin Gwynn via H.E. Heldal), RIFE-reports (1996-2010)
La Hague	~130	(data provided by Justin Gwynn via H.E. Heldal; OSPAR-reports)
Global fallout	~180-200 (included local fallout)	(Salbu and Holm, 2005)

1.4 Technetium-99 in the marine environment

1.4.1 Transport of ^{99}Tc in the marine environment

Transport of radionuclides depends on the location and way they are being introduced into the oceans. When it comes to radionuclides discharged from point – sources (like reprocessing discharges) the initial dilution will depend on factors like density, depth of release, tidal and eddy currents, wave actions and wind. Once the radionuclides are incorporated in the seawater, local currents will advect them away from the source and turbulent motion will contribute to the dispersion (Vintró et al., 2001).

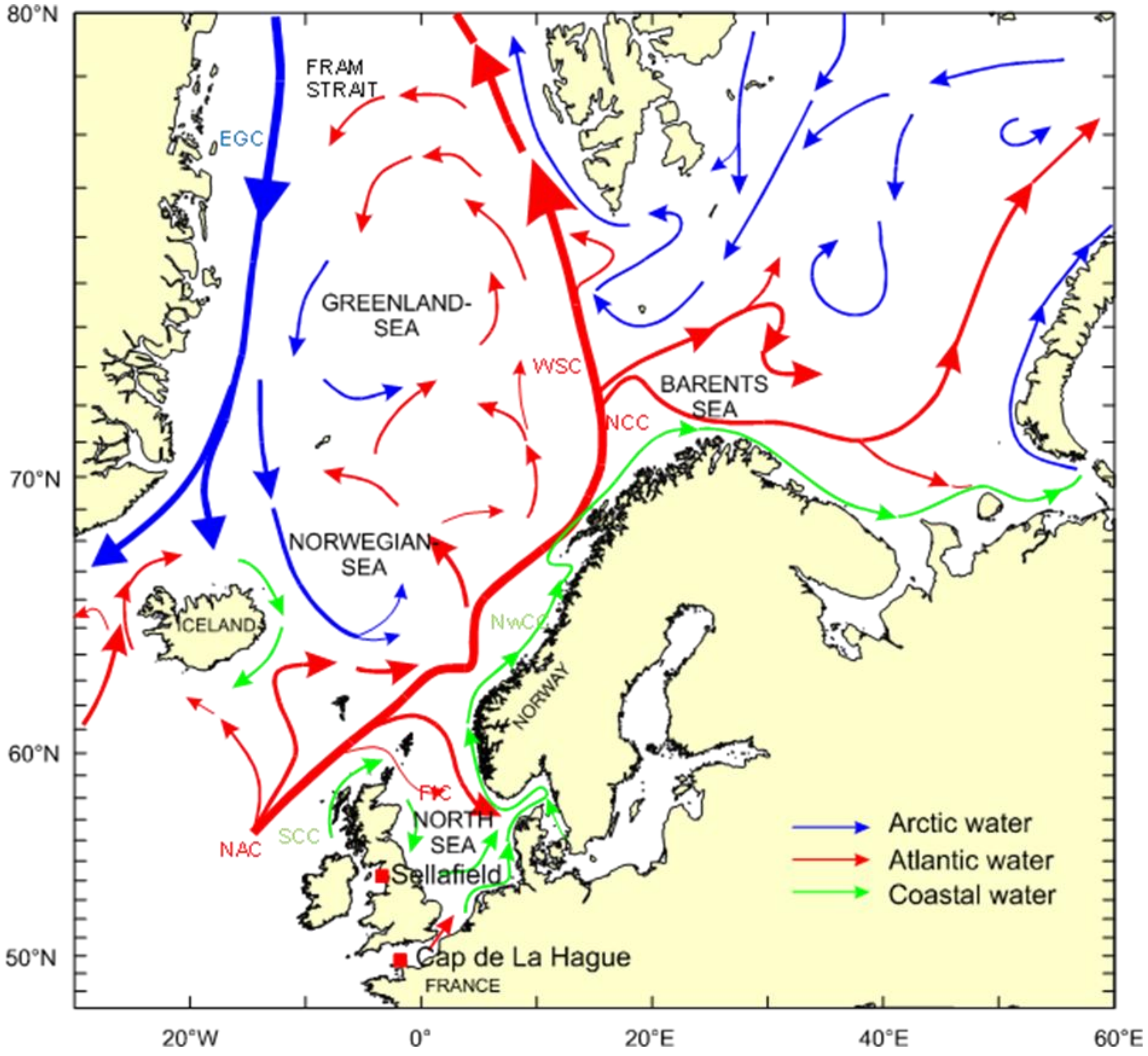

Figure 1.6: Circulation of surface waters of the North, Norwegian, Greenland and Barents Seas.

The pathway of conservatively radionuclides like ^{90}Sr, ^{99}Tc, ^{129}I, ^{137}Cs and ^{134}Cs from Sellafield to the Arctic has been described in many studies and is summarized by e.g. Kershaw and Baxter (1995) and Kershaw et al. (2004). The main circulation pattern of surface waters in the Nordic Seas is shown in figure 1.6. Assuming that ^{99}Tc from Sellafield follows the general circulation pattern of surface waters shown in figure 1.6; the initial plume is carried northwards out of the Irish Sea, via the North Channel and along the coast of Scotland in the Scottish Coastal Current (SCC). At the entrance of the North Sea, off the Scottish coast, the coastal water labelled with ^{99}Tc originating from Sellafield, is mixed with high salinity Atlantic water (AW) from the North Atlantic Current (NAC). Sellafield radionuclides are transported into the northern part of the North Sea both via the Pentlands Channel and in the Fair Isle current (FIC) between Shetland and Orkney. ^{99}Tc originating from Sellafield is then transported southwards to the central and southern parts of the North Sea. The water masses are then partly transported east in the FIC, and partly further to the south. The southern proportion will eventually merge with water from the English Channel, containing radionuclides from La Hague near the entrance of the Skagerrak. This water will mix with lower salinity containing outflow from the Baltic Sea and fresh water runoff from land. Together these water masses form the Norwegian Coastal Current (NwCC), which flows northwards along the Norwegian coast. The NwCC splits in two branches off the coast of northern Norway; one narrow branch goes along the coastal side and the other branch goes further offshore and runs parallel to eastern branch of the Norwegian Atlantic Current (NwAC). Atlantic water progressively mixes with the NwCC, causing dilution of the ^{99}Tc signal in the NwCC and contamination of the NwAC. At the western boundary of the Barents Sea (about 70°N) the NwAC splits into two currents; the North Cape Current (NCC) flowing eastwards into the Barents Sea, and the West Spitsbergen Current (WSC) which flows northwards. The WSC passes through the Fram Strait into the Nansen Basin. A return flow goes via the East Greenland Current (EGC), the Denmark Strait overflow and the Faroe Bank Channel overflow. (Kershaw and Baxter, 1995, Kershaw et al., 2004).

1.4.2 Transit times and transfer factors

By comparing seawater activity concentrations with discharge data from a point-source, one can calculate transit times (transport times) and transfer factors (TFs).

The transit time, *t*, is defined as the time between a specific discharge and the occurrence of the maximum activity concentration from that discharge reaching the sampling location

(Dahlgaard, 1995). Figure 1.7 shows indicated transit times from Sellafield (Dahlgaard, 1995). The estimated transit time from Sellafield to the North and Barents Seas is 3 and 5-6 years, respectively (figure 1.7). However, initial observations of EARP-related ^{99}Tc indicated more rapid transit times, with a transit time of 9 months to the Pentlands (entrance to the northern North Sea) (Leonard et al., 1997). Table 1.3 shows estimated transit times from Sellafield to different locations based on radiocaesium (left column) and EARP-related ^{99}Tc (right column).

A transfer factor (TF) is defined as the ratio between the observed environmental concentration at a given remote location and the average amount discharged from a point-source *t* years earlier (*t* is the average transit time to the location). The units for TFs are usually given as Bq m^{-3} / PBq yr^{-1} (Kershaw et al., 2004). TFs indicate the degree of dilution of the tracer signal and can be used as a measure of the dispersion, while the transit time is a measure of advection (Kershaw et al., 2004). Brown et al. (1999) estimated the transit time to the Norwegian south-west coast to be around 2.5 years and the TF to be approximately 20 Bq m^{-3} / PBq a^{-1}. Brown et al. (2002) calculated the transit time for ^{99}Tc from Sellafield to the sampling location Hillesøy (Troms, Northern - Norway), to be 42 months (3.5 years), and a transfer factor of 6 Bq m^{-3} per PBq yr^{-1}. This means, for example, that a ^{99}Tc discharge from Sellafield of 100 TBq (0.1 PBq), will give a theoretical seawater concentration near Hillesøy of approximately 0.6 Bq m^{-3} 42 months later.

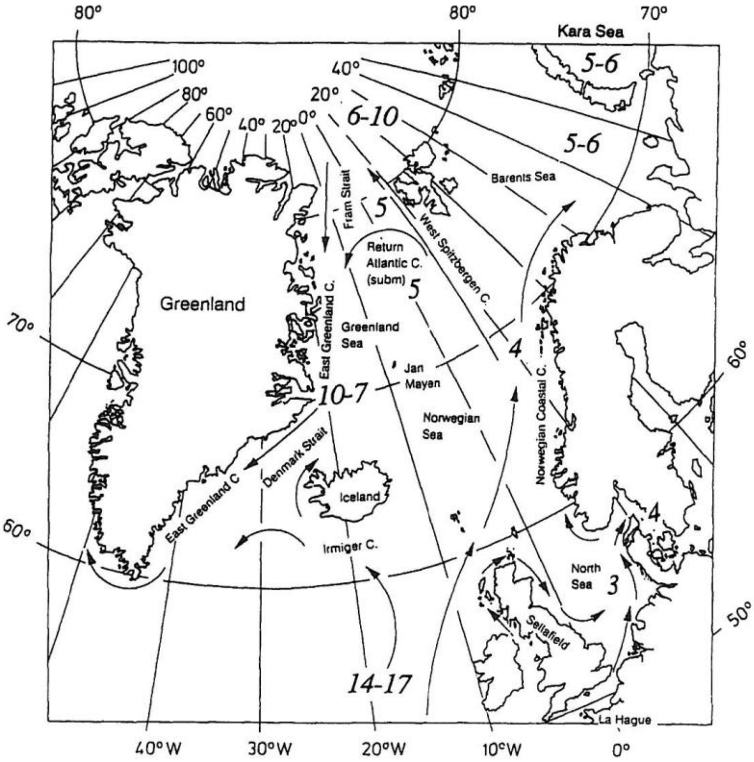

Fig. 3 Major surface currents and transit times in years from Sellafield to different sea areas. The indicated transit time (14–17 years) for the North Atlantic Current is deduced from Dickson *et al.* (1988) relative to the East Greenland Current Polar Water.

Figure 1.7: Transit times (in years) from Sellafield to different sea areas. Transit times from La Hague will be two years earlier (Dahlgaard, 1995).

Table 1.3: Transit times from Sellafield to different locations

Location	**Transit time (years) based on radiocaesium from Sellafield**	**References**	**Transit time for EARP-related ^{99}Tc from Sellafield**	**References**
North Channel (UK)	1	(Kershaw and Baxter, 1995)	~3 months	(Leonard et al., 1997, McCubbin et al., 2002)
North Sea	3	(Dahlgaard, 1995)		
Pentlands			~9 months	(McCubbin et al., 2002)
Norwegian Coastal Current	3-4	(Dahlgaard, 1995)	2.5 years	(Brown et al., 1999)
Barents Sea	5-6	(Dahlgaard, 1995)		
Hillesøy (Troms, Northern - Norway),			3.5 years	(Brown et al., 2002)
Fugløya			4.5 years	(Kershaw et al., 2004)

1.4.3 Seawater activity concentrations of ^{99}Tc in different areas before and after EARP

The Irish Sea

Before 1994, the levels of ^{99}Tc were around 1-4 Bq m^{-3} for a large part of the Irish Sea (Leonard et al., 1997). As a consequence of the elevated ^{99}Tc discharges from Sellafield following the commissioning of EARP, McCubbin et al. (2002) observed a record maximum seawater concentration of ^{99}Tc of approximately 1800 Bq m^{-3} close to the Sellafield pipeline in 1995. In 1998 the concentration at the same sampling location was approximately 40 Bq m^{-3}. McCubbin et al. (2002) stated that activity concentrations post-EARP was elevated by more than one order of magnitude compared with pre-EARP observations for the Irish Sea.

The North Sea

Leonard et al. (1997) measured pre-EARP activity concentrations of ^{99}Tc of 0.1 – 0.2 Bq m^{-3} in the North Sea off the Scottish coast in 1992-1993. They also performed post-EARP measurements in the same region in December 1994, which showed enhanced levels of ^{99}Tc (0.2 -2.5 Bq m^{-3}). Herrmann et al. (1995) also reported pre-EARP levels (1990-1992) of ^{99}Tc in the North Sea generally lower than 1 Bq m^{-3}, with levels exceeding 1 Bq m^{-3} in the southern parts, near the English Channel, reflecting the impact of La Hague discharges. From 1996 until 1999, there was a general increase in activity concentrations of ^{99}Tc in the North Sea. The levels ranged from 0.9-8.5 Bq m^{-3} in November 1996 and 1.7-3.4 Bq m^{-3} in 1997 (Brown et al., 1998). In 1999, the reported levels of ^{99}Tc in the North Sea ranged from 0.46 – 7.2 Bq m^{-3} (Rudjord et al., 2001) and 0.1 – 6.8 Bq m^{-3} (Nies et al., 2000), with maximum concentration of around 7 Bq m^{-3} at the west coast of Denmark. Nies et al. (2009) measured ^{99}Tc concentrations of 0.13-2.08 Bq m^{-3} in the North Sea in 2005. The activity concentrations of ^{99}Tc in the North Sea in 2007 were in the range 0.17-1.5 Bq m^{-3}, with the highest concentration measured in a sample collected off the east coast of Scotland (NRPA, 2009).

The Skagerrak

Herrmann et al. (1995) reported ^{99}Tc levels in the Skagerrak in February 1991 (range 0.3-0.5 Bq m^{-3}), November 1991 (range 0.5-0.8 Bq m^{-3}) and November 1992 (range 0.1-0.6 Bq m^{-3}).

The Norwegian Coastal Current

Herrmann et al. (1995) reported pre- EARP ^{99}Tc levels of 0.4 Bq m^{-3} in Norwegian coastal waters in July 1991. The average seawater activity concentration of ^{99}Tc on the Norwegian south west coast in 1996 was 3.4 Bq m^{-3} (Brown et al., 1999). ^{99}Tc activity concentrations are generally relatively high in the Norwegian coastal current, compared to open sea areas, reflecting circulation patterns of surface water.

The Norwegian Sea

Kershaw et al. (1999) measured the concentration of ^{99}Tc in the Norwegian Sea and the Barents Sea in 1994 (before the EARP plume reached this area). They measured concentrations in the range from 0.04-0.12 Bq m^{-3} in the Norwegian Sea. The highest concentration (0.12 Bq m^{-3}) was observed in the NwCC. In 2006, the ^{99}Tc concentration level ranged from < 0.04 – 0.8 Bq m^{-3} in the Norwegian Sea (NRPA, 2008). The highest concentration was observed in the NwCC.

The Barents Sea

In 1994, activity concentrations of ^{99}Tc in the Barents Sea were generally below 0.1 Bq m^{-3}, with a maximum concentration of 0.14 Bq m^{-3} observed in the NwCC near Fugløya (Kershaw et al., 1999). In July 1998 the ^{99}Tc concentration near Fugløya was measured to 0.86 Bq m^{-3}, approximately 6 times higher than the "background" level observed in 1994 (Kershaw et al., 2004). Kershaw et al. (2004) therefore estimated the EARP-related transit time from Sellafield to Fugløya to be approximately 4.5 years. In July 1999, the ^{99}Tc concentration near Fugløya had increased to 1.49 Bq m^{-3}; one order of magnitude higher than the 1994 level (Kershaw et al., 2004). During recent years, the levels have decreased. In 2007, activity concentrations of ^{99}Tc in the Barents Sea ranged from 0.06 – 0.26 Bq m^{-3} (NRPA, 2009).

Activity concentrations in the Barents Sea are lower compared to levels in the North Sea, due to transport time and dilution of the tracer signal when the NwCC mixes with ^{99}Tc poor, salinity rich Atlantic Water.

Hillesøy, Troms

In July 1997 NRPA began monthly sampling of surface seawater and seaweed at Hillesøy in Troms, analyzing for ^{99}Tc. Figure 1.8 shows average seawater concentrations of ^{99}Tc at Hillesøy, along with annual discharge data from Sellafield. The peak value for the average seawater concentrations observed in 1999, was 1.46±0.30 Bq m^{-3} (Kolstad and Lind, 2002). Similar values were observed in 2000 and 2001 (1.42±0.34 and 1.25±0.33 Bq m^{-3}, respectively) (Kolstad and Lind, 2002). In 2004 the average value was 0.82 Bq m^{-3} (NRPA, 2006). The small peak in 2005 (0.88±0.10 Bq m^{-3}) (NRPA, 2007) could be a response to the relatively high discharge from Sellafield in 2001 and 2002. During recent years a decrease in seawater concentrations at Hillesøy is observed, this trend is seen in figure 1.8. In 2006 the average activity concentration in Hillesøy seawater was 0.61±0.10 Bq m^{-3} (NRPA, 2008), which is at the same level as the concentration observed in July 1997. In 2007 the average concentration was 0.5 ± 0.1 Bq m^{-3} (NRPA, 2009).

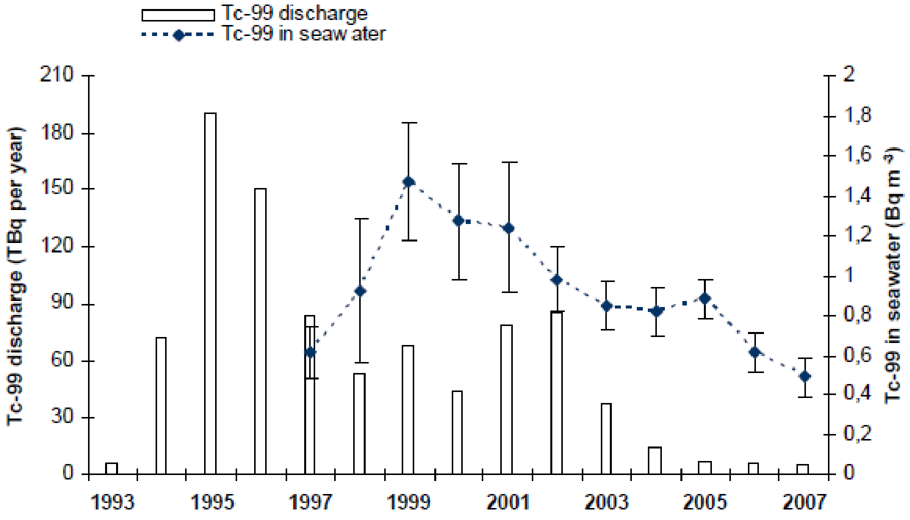

Figure 1.8: Annual discharge of ^{99}Tc from Sellafield together with annual average activity concentration (Bq m^{-3}) of ^{99}Tc in seawater at Hillesøy in Troms from monthly sampling conducted by NRPA. From NRPA (2009).

1.4.4 Uptake of ^{99}Tc in marine organisms

The uptake of ^{99}Tc in marine organisms is generally low, except for brown seaweeds and lobsters (e.g. Brown et al., 1999, Smith et al., 2001, IAEA, 2004). As a result of the discharges from Sellafield, elevated levels of ^{99}Tc were observed in these species along the Norwegian coast (e.g. Brown et al., 1999). The uptake of ^{99}Tc from seawater for these marine organisms will be discussed in chapter 4.2.1, in relation to the ^{99}Tc activity concentrations in seawater presented in this study, and hypothetical discharge scenarios.

1.5 Monitoring radioactive contamination in the marine environment

The activity concentrations of ^{99}Tc in Norwegian marine waters have been closely monitored within the Norwegian national monitoring programme RAME (Radioactivity in the Marine Environment) from the time when enhanced levels first were observed in 1996. RAME is coordinated by the Norwegian Radiation Protection Authority (NRPA) and funded by the Ministry of Environment. The Institute of Marine Research (IMR) has participated in RAME since 1999. Each year, a cruise conducted by IMR with collection of seawater, sediments and marine organisms in Norwegian coastal waters and adjacent seas is performed, in order to document levels and trends of radionuclides in the Norwegian marine environment. The cruise that includes sample collection for the RAME programme is circulating between the Barents Sea, Norwegian Sea and the North Sea / Skagerrak. The results from the RAME programme are presented in annual reports from the NRPA (Brungot et al., 1999, Rudjord et al., 2001, Kolstad and Lind, 2002, NRPA, 2004, NRPA, 2005, NRPA, 2006, NRPA, 2007, NRPA, 2008, NRPA, 2009, NRPA, 2011).

1.6 The use of radionuclides in validation of oceanographic models

Conservative radionuclides are soluble and are transported by ocean currents without being affected by other processes. They can therefore travel long distances from the point-source without being deposited on the seabed. For these radionuclides, predictions can be made using hydrodynamic models (Vintró, 2009). Conservatively behaving radionuclides can therefore be valuable as oceanographic tracers in order to validate simulated circulation and dispersion scenarios. Controlled discharges of anthropogenic radionuclides from reprocessing plants are suited for this purpose since the release function is known and the fate of the radionuclides are well monitored. In addition, it is possible to measure extremely low concentrations of radioactivity in seawater. Observations of e.g. ^{137}Cs (e.g. (Harms and Karcher, 2003) and ^{99}Tc (e.g. (Karcher et al., 2004) activity concentrations in the Nordic Seas have been used to validate models, by comparing observations of radionuclide activity concentrations with model-predictions. Karcher et al. (2004) compared model results of simulated ^{99}Tc dispersion in the Nordic Seas with observations from 1996 to 1999 in order to study surface concentrations, pathways and transit times of EARP-related ^{99}Tc discharged from Sellafield. They used a hydrodynamic model and an assessment box-model, and found that their model was able to simulate the dispersion of ^{99}Tc realistically.

One of the objectives (objective 3) with this study is to obtain a data set that can be used to validate the oceanographic model ROMS (Regional Ocean Modeling System). ROMS is a free-surface, terrain-following, primitive equations ocean model (Haidvogel et al., 2008, myroms, 2011). This model is currently used by oceanographers at IMR for example to simulate releases of radioactive contamination from the Russian submarines “Komsomolets” and “K-159”, which sank south-west of Bear Island and outside the Kola coast, respectively (H.E. Heldal, pers. comm.). In the continuation of this work, it is planned to use ROMS for modelling the dispersion of discharges from Sellafield. This validation of ROMS will be done by comparing the measurements of ^{99}Tc in seawater in the period 1998-2010 with model results, and evaluate how well the model results corresponds with observations. The ultimate aim with this work will be to develop a tool for evaluating the consequences for marine organisms and ecosystems following a hypothetical accidental release of radioactive pollution in the future (H.E. Heldal, pers. comm.).

2. Materials and methods

2.1 Sample collection

2.1.1 The cruise with R/V Johan Hjort during the summer 2010

The sample collection was carried out in the North Sea and Skagerrak with the research vessel *R/V Johan Hjort* during the period 3 July to 2 August 2010. One of the objectives of the cruise was to collect samples of seawater, sediments and marine organisms for subsequent analyses of various organic contaminants and radionuclides, including collection of seawater for ^{99}Tc analysis. Scientists from IMR, NRPA and the International Atomic Energy Agency (IAEA) participated. The cruise was divided into two parts. The first part (3 July – 21 July) included stations in the southern part of the northern North Sea, Skagerrak and the east coast of Britain. The second part (21 July – 2 August) included stations from the northern part of the North Sea (above 60°N). In figure 2.1, a map of the cruise is shown. The position, depth and sampling dates of the samples collected are presented in table 2.1. All sampling locations, except "station X", were determined by scientists from IMR, NRPA and IAEA prior to the cruise. Station X was an "extra" sampling location in Skagerrak, chosen in order to get a complete transect in the region between Oksøy (south of Kristiansand) and Hanstholm. Sampling locations marked with "T" are stations within a monitoring programme called "Tilførselsprogrammet"[3] coordinated by the Climate and Pollution Agency (Klif).

The author of this thesis participated in the first part of the cruise and was responsible for the collection of seawater samples for ^{99}Tc-analyses. A scientist from NRPA was responsible for the corresponding sampling during the second part of the cruise. A total of 20 samples were collected; 15 samples were collected from the first part of the cruise, and 5 samples were collected from the second part (table 2.1).

During the cruise, hydrographic data collection took place using a CTD-probe at each station, see figure 2.3 b). In addition, temperature and salinity in surface water was monitored continuously using a Thermosalinograph.

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[3] http://www.klif.no/Tema/Miljoovervakning/Statlig-miljoovervakning/Overvaking-av-miljogifter-og-beregning-av-tilforsler-til-norske-kyst-og-havomrader-Tilforselsprogrammet/

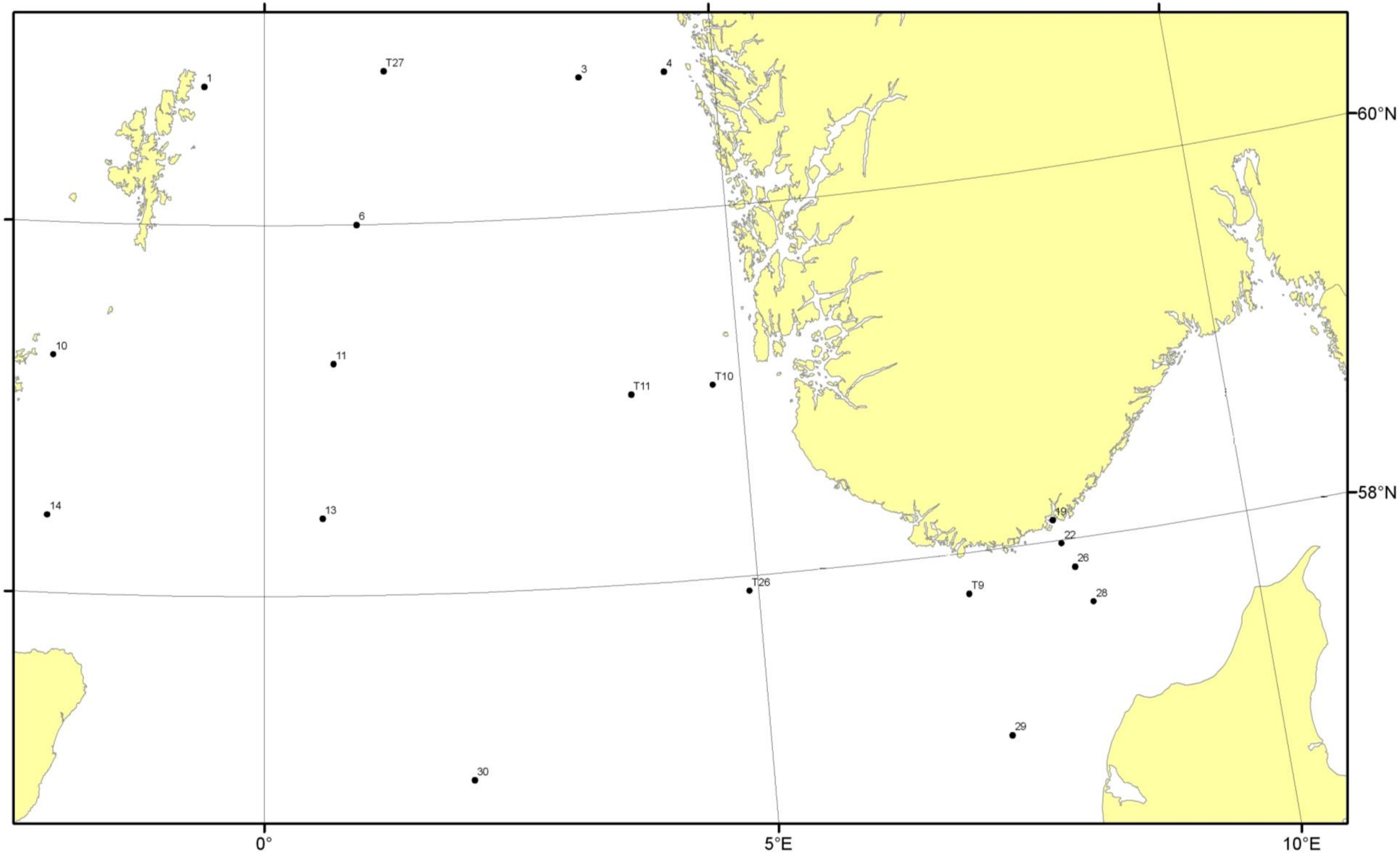

Figure 2. 1 Map of the *R/V Johan Hjort* cruise stations with all ^{99}Tc sampling locations (except station X).

Table 2.1: Position, depth and sampling date for all ^{99}Tc samples taken during the cruise with R/V Johan Hjort summer 2010. NwCC=Norwegian Coastal Current, ECB=East Coast of Britain

Station	Area	Sampling date	Sampling depth (m)	
T10	NwCC	05.07.2010	5	
T9	NwCC	06.07.2010	5	Two samples, Intercomparison with CEFAS
22	Skagerrak	07.07.2010	5	
19	Skagerrak	07.07.2010	5	
26	Skagerrak	08.07.2010	5	
28	Skagerrak	08.07.2010	5	
X	Skagerrak	08.07.2010	5	
29	North Sea	08.07.2010	5	
30	North Sea	10.07.2010	5	Two samples, Intercomparison with CEFAS
T26	NwCC	13.07.2010	5	
13	North Sea	15.07.2010	5	
14	North Sea	17.07.2010	5	
T11	NwCC	18.07.2010	5	
11	North Sea	19.07.2010	5	
10	North Sea/ECB	19.07.2010	5	
6	North Sea	26.07.2010	5	
3	NwCC	27.07.2010	5	
T27	North Sea	29.07.2010	5	
1	North Sea	31.07.2010	5	
4	NwCC	01.08.2010	5	

2.1.2 The study area

The North Sea, Skagerrak, and the Norwegian Coastal Current

The North Sea is shallow compared to the Norwegian and the Barents Sea. Approximately 2/3 of the North Sea is shallower than 100 metres (Gjøsæter et al., 2009). The deepest part of the Sea is the Norwegian trench, outside the Norwegian coast, with depths exceeding 700 metres in the Skagerrak (Sætre, 2007). The topography of the sea affects the circulation pattern of water masses. The water masses in the North Sea originate from the inflow of high salinity (>35) Atlantic Water (AW) from the Norwegian Sea in the north and through the English Channel in the south and fresh water runoff from rivers. The salinity of the surface waters in the North Sea is generally above 35 in the northern part, while in the south-western part the salinities are less, due to fresh water input from the continent (e.g. Otto et al. (1990). For further information about salinity and units, see Appendix 2.

The Norwegian Coastal Current (NwCC) originates primarily from the outflow of brackish water from the Baltic Sea and fresh water run-off from Norway (Sætre, 2007) which gradually mixes with water masses with higher salinity. The salinity of the Norwegian Coastal Water is below 35. Circulation features of the NwCC are shown in figure 2.2 b).

The water in the Skagerrak consists of three main water masses. Skagerrak Coastal Water (SCW) has salinities of 25-32 and temperatures between 0°C - 20°C, Skagerrak Water (SW) has salinities around 32-35 and temperatures between 3°C - 16°C and Atlantic Water with salinity above 35 and temperatures between 5.5°C and 7.5°C (Sætre, 2007). This high salinity, dense Atlantic water is seen as the deepest layer, underneath the less dense Skagerak water in the sub-surface layer. The thin surface layer consists of coastal water with salinities between 25 and 32. The properties of the mentioned water masses are listed in table 2.2.

The water circulation in the North Sea is mainly anti-clockwise and about 70 % of the water masses pass through Skagerrak before it continues northwards as a part of the Norwegian Coastal Current (Gjøsæter et al., 2009). The general circulation pattern of the Skagerrak is cyclonic or counter-clockwise (Sætre, 2007). The main circulation features of the North Sea and the Skagerrak are shown in figure 2.2 a). However, it is important to stress that this figure represents a climatic average situation. Significant seasonal and inter-annual variability in water circulation patterns in the Norwegian Coastal Current and the North Sea can occur due to changes in tides, wind conditions, variations in freshwater run- off from land and Baltic outflow, and variation in inflow of Atlantic Water (Sætre, 2007).

The boundary between the North Sea and the Skagerrak is considered as the line between Hanstolm in Denmark and Lindesnes in Norway. At IMR the section between Hanstholm and Oksøy (near Kristiansand) is used as an entrance line of the Skagerrak (Morten D. Skogen, pers. comm.). In the north, the boundary between the North Sea and the Norwegian Sea is considered to be at 62 °N (Stad) (Morten D. Skogen, pers. comm.). In this study, a division between the Norwegian coastal current north and south of Stad (62°N) is made.

Table 2.2: Definition of water masses and currents

Acronym	**Name**	**Salinity (psu[4])**	**Temperature (°C)**	**Reference**
AW	Atlantic Water	> 35.0	>5 12-14 (summer)	(Kershaw et al., 2004) (Otto et al., 1990)
NwCC	Norwegian Coastal Current	<34.8		(Kershaw et al., 2004)
SW	Skagerrak Water	32-35	3-16 14-17 (summer)	(Sætre, 2007) (Otto et al., 1990)
SCW	Skagerrak Coastal Water	25-32	0-20 14-17 (summer)	(Sætre, 2007) (Otto et al., 1990)

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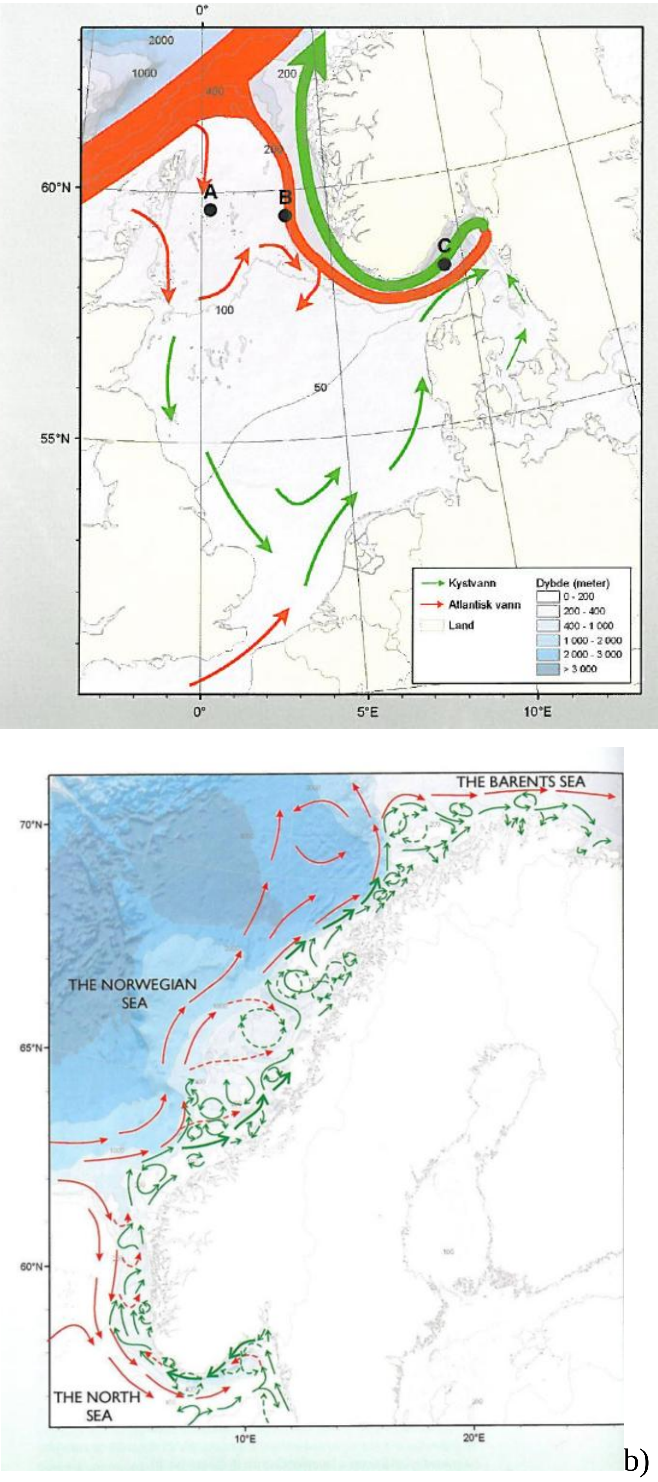
[4] psu= practical salinity unit. For further information, see Appendix 2



a)

b)

Figure 2.2: a) The main circulation features and bathymetry of the North Sea and the Skagerrak (Gjøsæter et al., 2009) Red arrows indicate Atlantic water, green arrows coastal water

b) Circulation features of the Norwegian Coastal Current. Red arrows indicate Atlantic water and green arrows the Norwegian Coastal Current (Sætre, 2007)

2.1.3 Collection and pre-treatment of seawater samples

Surface seawater samples of 100 L from a depth of 5 m were collected in 4 x 25 L polyethylene carboys using a shipboard pump. The sampling equipment is shown in figure 2.3 a). Since the samples were collected in open sea areas with low concentrations of suspended materials, filtering prior to analysis was not necessary. The accurate mass of each water sample was registered using a shipboard fish weight. A constant value of 1.025 kg dm^{-3} was used as a density factor for seawater when calculating the volumes of the seawater samples from the measured weights (volume = mass / density). This approximation will cause some error in the sample volumes; since the density of seawater depends upon both the temperature and the salinity of the water mass. (For further information about density of seawater, see Appendix 2). It is, however, assumed that this error is negligible when it comes to the activity concentration of ^{99}Tc, although it will inevitably add some uncertainty to the measurement. Furthermore, this density factor has been used at IMR in all previous ^{99}Tc determinations, and also at CEFAS. The volumes of the seawater samples have an estimated uncertainty of ± 0.1 L.

To each sample, 2 ml of a standard $KReO_4$ solution (0.5 ml $KReO_4$ solution per 25 L can), with a concentration of 4.00 mg Re ml^{-1}, which gives 8.00 mg Re per sample, was added as a yield monitor. See chapter 2.2 for details on the analytical method.

The sample was thoroughly mixed by bubbling air through it. After homogenization, the sample was passed through an anion exchange column (50 ml Amberlite IRA-400 in 50 ml polypropene syringes) using a peristaltic pump with a flow rate of approximately 2000 ml h^{-1}. Figure 2.4 show the procedure of pre-concentration. For each sample of 100 L, two anion exchange columns were used (one column is suitable for 50 L of seawater passing through). The columns were turned upside-down at a regular basis to get out air from the columns. The columns were marked with the name of the vessel, date, CTD-station, depth and number of column and stored in sealed plastic bags at room temperature aboard the vessel. The columns were transported to IMR immediately after the cruise for subsequent analysis at the chemistry laboratory.

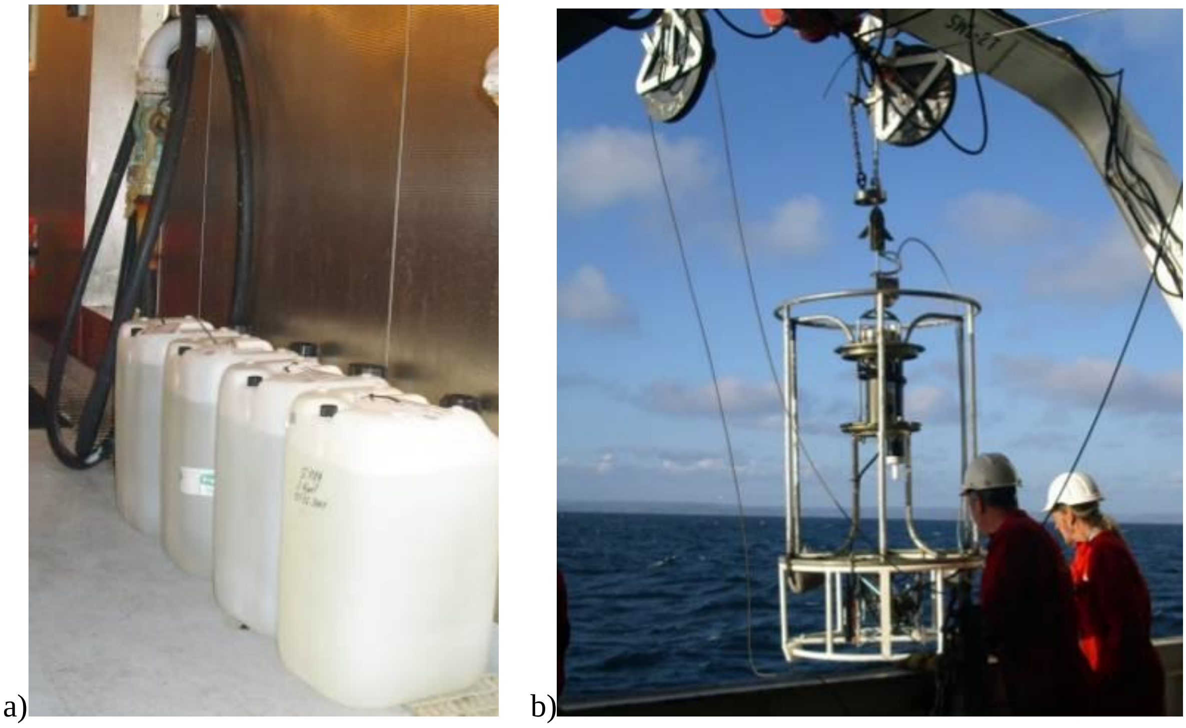


Figure 2.3: Pictures from the R/V Johan Hjort cruise. a) Collection of surface seawater in carboys aboard the ship. b) The CTD-probe for measurement of salinity, temperature and density is lowered into the sea.

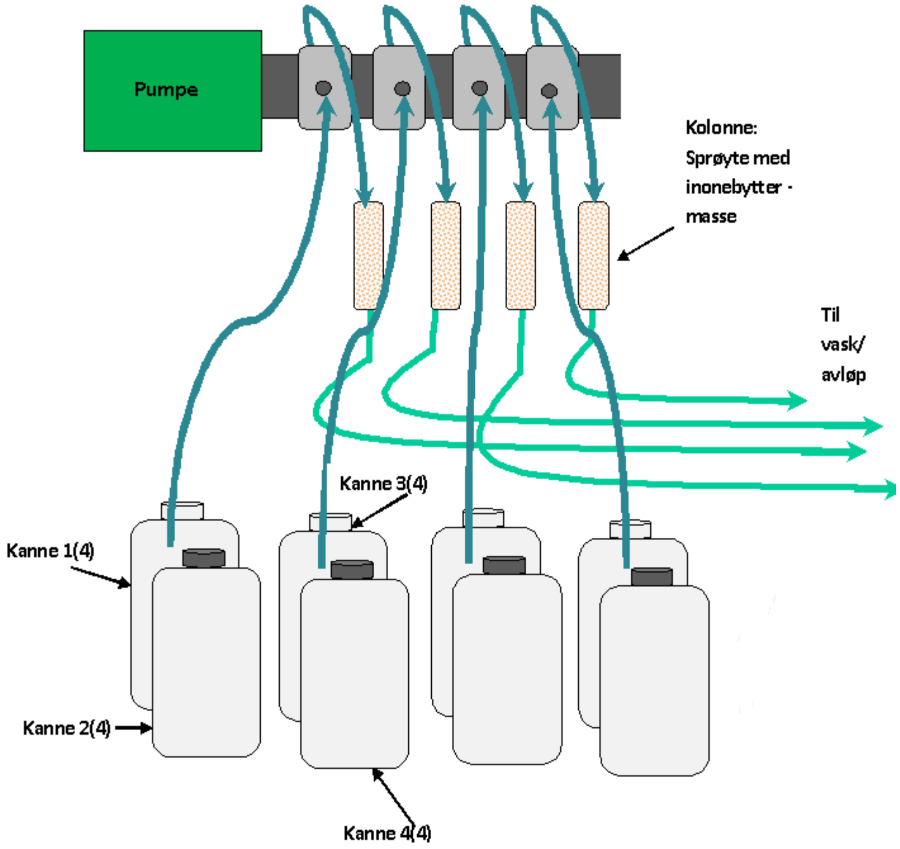


Figure 2.4: Schematic drawing of pre-concentration of seawater samples for ^{99}Tc analysis.

2.2 Determination of ^{99}Tc in seawater

The analytical method for determination of ^{99}Tc in seawater used at IMR (Heldal, 2009) is based upon (Harvey et al., 1991, Harvey et al., 1992) and close collaboration with Centre for Environment, Fisheries & Aquaculture Science (CEFAS)[5]. This method uses rhenium, in the form of $KReO_4$, as a non-isotopic carrier and yield monitor. After adding rhenium, a preliminary extraction of ^{99}Tc (and Re) based on anion-exchange separation is performed. The organic resin material is destroyed by muffle-ashing and the residue is dissolved. Iron hydroxide scavenging is thereafter performed to remove unwanted components such as alkaline and rare-earth elements and phosphates. ^{99}Tc and Re are further extracted by a second anion-exchange separation and eluted with an alkaline sodium perchlorate solution. Next, two subsequent sulphide precipitations are performed in order to remove perchlorate ions. Finally, the tetraphenyl arsonium salts of ^{99}Tc and Re are isolated. Perchlorate ions would also form an insoluble tetraphenyl arsonium salt, and needed therefore to be removed before the final precipitation. The yield of the rhenium tetraphenyl arsonium salt is determined gravimetrically and ^{99}Tc is beta-counted.

2.2.1 The radiochemical separation of ^{99}Tc from seawater

Principle

^{99}Tc is a low-energy pure beta emitter (E_{max} = 292 keV) decaying from ^{99}Mo, and a thorough radiochemical separation of ^{99}Tc from the sample matrix and other interfering β-emitting radionuclides, such as e.g. ^{103}Ru, ^{106}Ru and ^{110}Ag (Salbu and Holm, 2005), is necessary for quantitative analysis.

A schematic diagram of the analytical procedure is given in figure 2.5.

Reagents used in the analysis are listed in Appendix 3.

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[5] CEFAS, Lowestoft Laboratory, Pakefield Road, Lowestoft, Suffolk NR33 0HT, UK

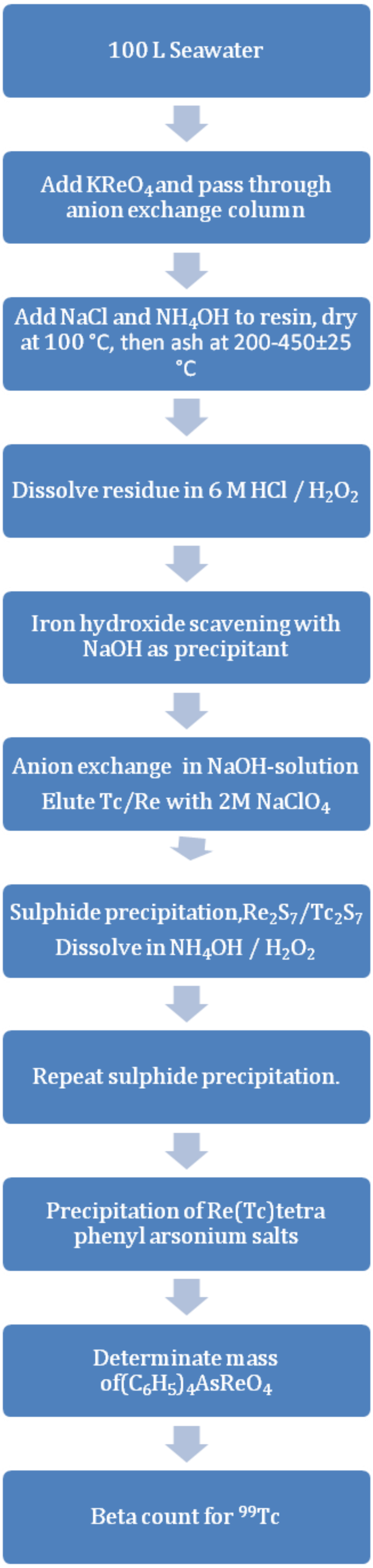


Figure 2.5: Schematic diagram of the analytical procedure for separating ^{99}Tc from the matrix

Quality Control

A dissolved sample of 81.2 g dried Fucus seaweed from CEFAS is used as a quality control (QC) in the analysis.

Pre-treatment of samples

In the laboratory, the resin was removed from the columns, transferred to a 600 ml heat resistant glass beaker marked using a heat resistant pen, and added 1 g NaCl. During each batch, 8 samples, one reagent blank (BLK) and one quality control (QC) were analyzed. To the beaker marked ‘QC’, 1 ml of ^{99}Tc quality control solution was added and 2 ml Re-solution were added to both BLK and QC. The sample was moistened thoroughly (~30-35 ml) with concentrated ammonium hydroxide, NH_4OH. (To BLK and QC: about 3 ml NH_4OH were added). Because of the volatility of the Tc(VII) oxidation state (vapour pressure of Tc_2O_7 at 100 °C ≈ 0.1 mmHg), technetium can easily be lost from warm oxidizing acidic solutions and during the dry ashing process, either as the heptoxide Tc_2O_7 or pertechnetic acid $HTcO_4$.The addition of ammonia solution (Foti et al., 1972 in Harvey et al., 1992) is thought to neutralize all the free acidic sites on the complex organic molecule present, thus help prevent the formation of the volatile acids $HTcO_4$ or $HReO_4$. Harvey et al. (1991) also showed that addition of sodium chloride to the mixture reduced the volatility of Tc and Re.

The samples were dried at temperature 100 ± 5 °C over night, and the organic resin material was destroyed by dry-ashing the samples in a furnace at a suitable temperature programme. In order to prevent loss of Tc and Re during the dry ashing process, the temperature was raised slowly from 200 to 450 °C over a period of 6 days.

Iron hydroxide ($Fe(OH)_3$) –scavenging

After dry-ashing, the sample was dissolved in a mixture of 50 ml 6 M HCl, 1 ml Fe^{3+} solution and 2 ml H_2O_2 by warming on a hotplate for about 15 minutes. (H_2O_2 was added in order to maintain Tc in the oxidized, heptavalent state.) The solution was made alkaline by adding approximately 55 ml of 6 M NaOH (controlled with pH-paper to make sure the pH was ~ 13-14) and 2 ml H_2O_2 was added. The solution was boiled on a hotplate for about 30 minutes and iron hydroxide, $Fe(OH)_3$ (s), was precipitated. Iron hydroxide acts like a scavenger, as it removes various potentially interfering radionuclides and matrix contaminants, such as alkaline and rare-earth elements and phosphates. Scavengers refer to the addition of reagents which form a precipitate with a large surface area, having charged active sites. Iron hydroxide is an effectively scavenger, having large surface area and positively charged active sites.

The sample was diluted to 150 ml with distilled water and cooled over night in a fume hood.

Anion-exchange in NaOH solution. Elution of Tc / Re with 2M $NaClO_4$

The sample was added to a funnel containing a 240 mm Whatman No. 542 filter paper. The funnel was attached to an anion exchange column (approximately 1.5 ml BioRad AG 1x8 (100-200 chloride) in a 14 cm long Pasteur pipette with internal diameter of 6 mm containing a small plug of glass wool to support the resin) by means of a piece of plastic tubing. The column had been rinsed with a few ml of distilled water, followed by some ml of 2 M NaOH, in order to make the resin alkaline before adding the sample through the filter. When the sample had passed through, the column was washed with 2 x 50 ml of 2 M NaOH. The filter with precipitate was discarded after the first 50 ml had passed the anion exchange column. All the raffinate and washing were discarded. The anion exchange resin has extremely high affinity for ReO_4^- and TcO_4^- under neutral or alkaline conditions ($K_d \approx 10^4$) (Harvey et al., 1992). Tc and Re were eluted from the column with 150 ml sodium perchlorate solution (0.3 M NaOH / 0.15 $HClO_4$). The eluate was collected in a marked, clean 250 ml beaker, covered with a watch glass and placed in a fume hood over night.

The first sulphide precipitation

The eluate was acidified by adding 30 ml of concentrated HCl and heated to boiling on a hotplate for 10-15 minutes in order to remove traces of H_2O_2. Approximately 1.6 g (between 1.55 and 1.65 g) of thioacetamide (CH_3CSNH_2) was thereafter carefully added. A black precipitate of Re_2S_7 / $^{99}Tc_2S_7$ was formed. The solution was maintained at 80-90 °C for 10-15 minutes in order to coagulate the precipitate. Then the precipitate of Re_2S_7 / $^{99}Tc_2S_7$ was filtered off onto a 47 mm 0.45 µm membrane filter contained in a 250 ml Millipore filtering assembly. The precipitate was washed with 2 x 100 ml distilled water, and the filtrate was discarded. The precipitate of Re_2S_7 / $^{99}Tc_2S_7$ was dissolved in a boiling mixture of 50 ml concentrated NH_4OH and 10 ml H_2O_2. (A small remainder of an insoluble sulphur compound was usually left on the filter; this was discarded together with the filter.) The resulting solution was transferred to a clean 250 ml beaker, heated on a hotplate until the volume was reduced to 20-30 ml, diluted to 150 ml with distilled water and left in a fume hood over night.

The second sulphide precipitation

The solution was added 15 ml concentrated HCl and heated to boiling to remove traces of H_2O_2. The sulphide precipitation was repeated as described above, the only change being that after volume reduction the solution was diluted to 50 ml with distilled water and cooled in a refrigerator over night.

Figure 2.6 shows pictures from the analytical procedure. In figure 2.6 a) the black sulphide precipitate can be seen.

Precipitation of Re (Tc) tetraphenyl arsonium salts

While swirling the beaker, 16 ml of a cold tetraphenyl arsonium chloride solution ($(C_6H_5)_4AsCl{\cdot}H_2O$) was added slowly to the cold solution. A white / pale blue precipitate was formed. This precipitate of tetraphenyl arsonium perrhenat / pertechnetate was filtered off onto a tared 0.45 µm 25 mm filter membrane having an outer hydrophobic ring (figure 2.6 b). The beaker and filter was thoroughly washed with distilled water. The membrane with the precipitate was placed on a piece of paper and then dried in a vacuum desiccator over night.

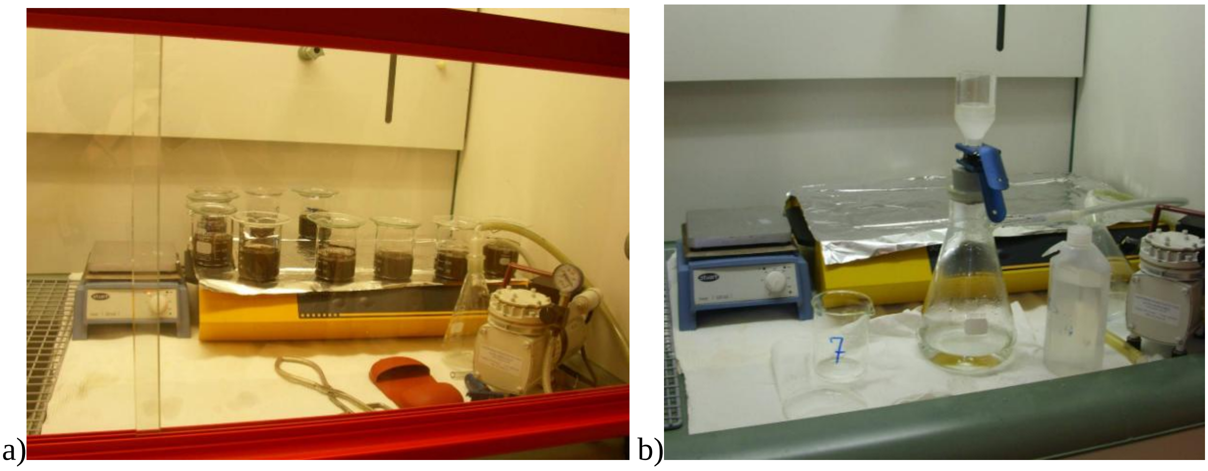


Figure 2.6: Pictures from the analytical procedure. a) Sulphide preciptiation of the samples. b) Filtering of the tetraphenyl arsonium perrhenat/pertechnetate salt onto a tared filter membrane.

2.2.2 Gravimetrical determination of yield and source preparation

After drying, the weight of the Re(Tc) tetraphenylarsonium salt, $(C_6H_5)_4AsReO_4$, was determined and the chemical yield calculated from the percentage recovery of rhenium. The sources were weighed using an analytical balance (Mettler AE-163) with an accuracy of four decimals.

The filter membranes with precipitate were mounted onto 25 mm plastic counting discs with rings, see figure 2.7. This was the final source.

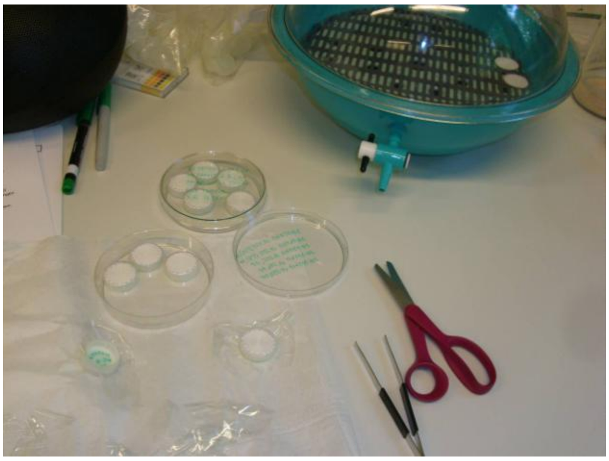


Figure 2.7: Preparation of the final sources

2.2.3 Radiometric determination of ^{99}Tc

Beta$^-$ - decay

Beta$^-$ - decay occurs when the N/Z ratio of the nuclide is too high (it has too many neutrons). Therefore, in beta$^-$ decay, a neutron is transferred into a proton and an electron (beta particle), and a new element is formed. The proton number, Z, increase with 1, the neutron number, N, decrease with 1 while the mass number, A, stays constant. The process can be written:

$${}^{A}_{Z}X \rightarrow {}^{A}_{Z+1}X + {}^{0}_{-1}\beta + \nu *$$

(Mother nuclide → daughter nuclide + β^- particle + antineutrino (ν*))

Beta radiation (β^-) exhibits a range of energies, and we get a continuous energy spectrum with a characteristic maximum energy (E_{max}), as shown in figure 2.8. E_{max} is shared between the beta particle and the antineutrino.

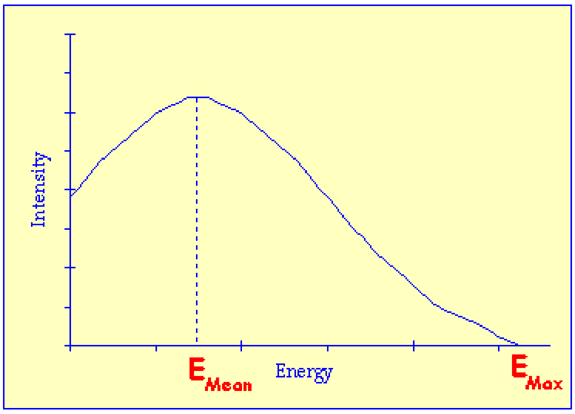


Figure 2.8: Beta energy spectrum. (Source: http://upload.wikimedia.org/wikibooks/en/5/5e/NM6_1.gif)

β^- radiation can be measured by using a beta counter, such as a Geiger-Müller (GM) counter or a liquid scintillation counter (LSC). For the analysis of environmental samples, a low level GM-counter is required. In a low-level GM counter the background is reduced by using lead shielding and a guard detector above the sample detector operating in anticoincidence mode with the sample detectors (Hou and Roos, 2008).

Geiger-Müller (GM) counters

When a sample containing a beta emitter is placed close to the window in a GM-counter, the gas will be ionized by the interaction with the beta radiation (electrons) and an electric current is established between the positive and negative electrodes. The electric pulse is registered and multiplies within the electronic circle. The signals are registered as counts and the number of counts (intensity) is proportional to the activity concentration of beta emitters in the sample.

Because of the continuous energy spectrum of the beta particles, radiochemical separation of the nuclide of interest from all other interfering radionuclides is required prior to counting. Samples for GM counting need to be prepared as thin sources in order to minimize self-absorption in the sample and obtain high counting efficiency (Hou and Roos, 2008).

The noble gas argon, Ar, is commonly used as GM counting gas. A problem is repetitive pulses due to secondary electron release by the positive ions as they reach the negative electrode (the cathode). To avoid this unwanted multiple firing of the counter, a small amount of a organic molecule, such as e.g. ethanol, isobutane, or ethyl formate, acting as a quenching agent, is added to the counting gas.

Because the ionization potential of the organic molecule is lower than that of Ar, when the positive argon ions moves to the negative electrode and encounters organic molecules (e.g. isobutane (2-methyl propane)) the following reaction occurs:

$$Ar^+ \quad + \quad CH(CH_3)_3 \rightarrow Ar \quad + \quad CH^+(CH_3)_3$$

The charge of the argon ion is transferred to the organic molecule which gains an electron upon striking the cathode. The energy released in the neutralization of the positive ions at the cathode causes dissociation of the quench gas molecules into uncharged fragments rather than producing secondary electrons at the cathode (Choppin et al., 2002, Ehmann and Vance, 1991).

RISØ low-level beta GM multicounter system

The sources were beta-counted using a low-level beta GM multicounter system model RISØ GM-25-5. The RISØ low-level beta multicounter system consists of a gas-flow unit which incorporates five individual GM sample counters and a guard counter, see figure 2.9, and an electronic system for treatment of the signals produced by beta particles in the GM multicounter, as shown in figure 2.10. The function of the guard counter is to reduce the cosmic ray background by using anticoincidence technique. The counter gas is the noble gas argon, Ar, (99 %) mixed with 1 % iosbutane. Isobutane act as a quenching agent. A flow diagram of the counter gas connections to the multicounter GM-25-5 is shown in figure 2.11. The sample sources (25 mm diameter) are inserted into the multicounter using a sample slide with five sample holders allowing five samples to be measured simultaneously. A lift slide is placed underneath the sample slide in order to minimize the distance between the sample and the counter window, thus optimizing counting efficiency.

In order to reduce background radiation, the multicounter is placed inside a lead shielding of 100 mm thickness. Furthermore, the counting room at IMR has low background. Low background radiation, gives a low limit of detection. The signals produced by beta particles in the GM multicounter are amplified and sent to a discriminator/anticoincidence module that eliminate background counts caused by cosmic radiation. The counts are obtained by a microprocessor and transferred to a PC via a USB interface. A pulse-height analyzing system is automatically controlling the high voltage supply. The GM-25-5 software controls start/stop, preset time, number of cycles and pulse height analyzing functions. Data files can be stored for further calculations and analysis (RISØ, 2009).

A standardized ^{99}Tc solution from NPL (National Physical Laboratory), Teddington, UK has been used to calibrate the beta-counter (Heldal, 2009).

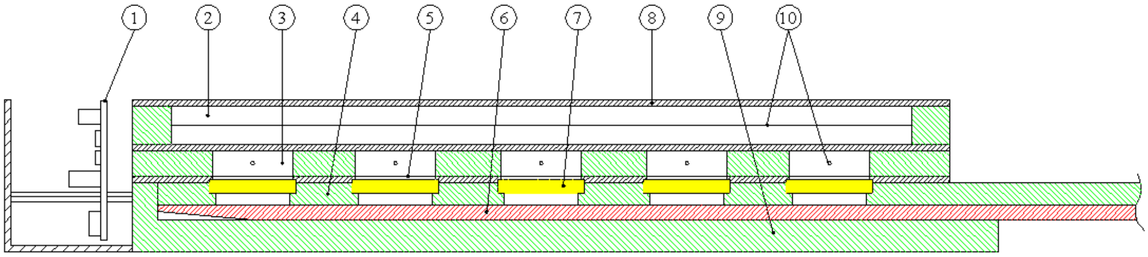


Figure 2.9: The five-sample beta GM multicounter, schematically. (1) Preamp., (2) Guard counter, (3) Sample counter, (4) Sample slide, (5) Mylar window, (6) Lift slide, (7) Sample, (8) Cu plate Acrylic frame, (9) Acrylic frame, (10) Anodes. Source: RISØ (2009).

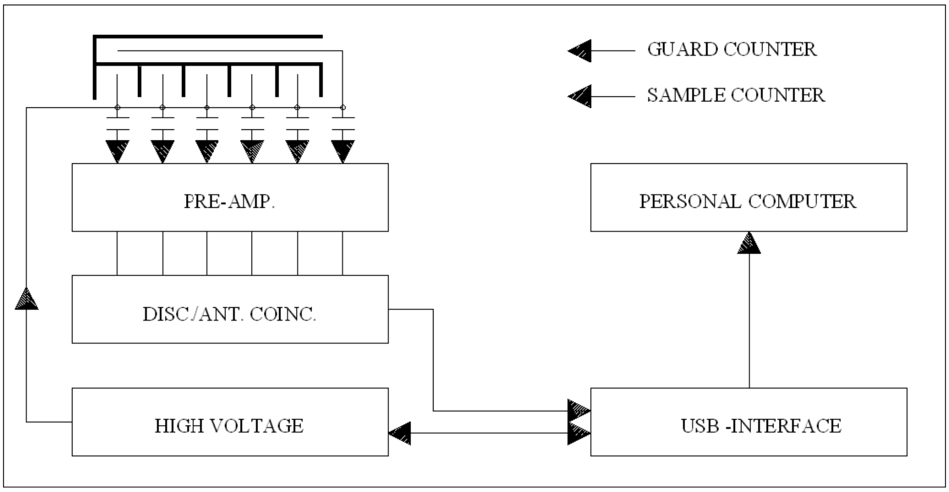


Figure 2.10: Block diagram of the electronics for the five sample multicounter. Source: RISØ (2009).

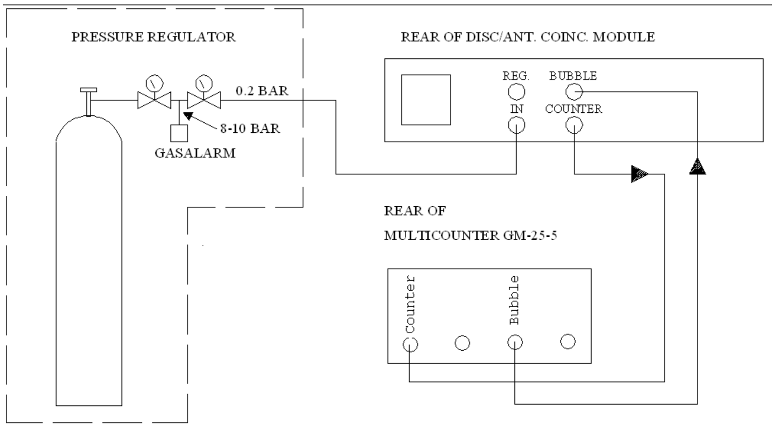


Figure 2.11: Flow diagram of the counter gas connections to the multicounter GM-25-5. Source: RISØ (2009).

Count times were in the order of 48 hours and all counts were corrected for background. Table 2.3 shows the average background count rate (counts per second, cps) for filter blanks on each of the five detectors in 2010. The average backgrounds in 2010 were between 0.0023 and 0.0025 cps. Figure 2.12 displays the variation in background in 2010 for the five detectors graphically. All calculations were performed using Microsoft Excel.

Table 2.3: Background control. Monthly measurements of filter blanks and calculation of average background count rate (cps) for each of the five detectors in 2010.

Date	**13.01.10**	**04.03.10**	**27.04.10**	**21.05.10**	**02.07.10**	**13.08.10**	**19.11.10**	**Average 2010**
Detector	cps	cps	cps	cps	cps	cps	cps	cps
1	0,0026	0,0024	0,0027	0,0021	0,0024	0,0023	0,0027	**0,0025**
2	0,0022	0,0021	0,0022	0,0023	0,0021	0,0024	0,0024	**0,0023**
3	0,0023	0,0023	0,0022	0,0024	0,0024	0,0022	0,0024	**0,0023**
4	0,0023	0,0023	0,0022	0,0023	0,0023	0,0021	0,0023	**0,0023**
5	0,0026	0,0024	0,0024	0,0023	0,0024	0,0025	0,0025	**0,0024**

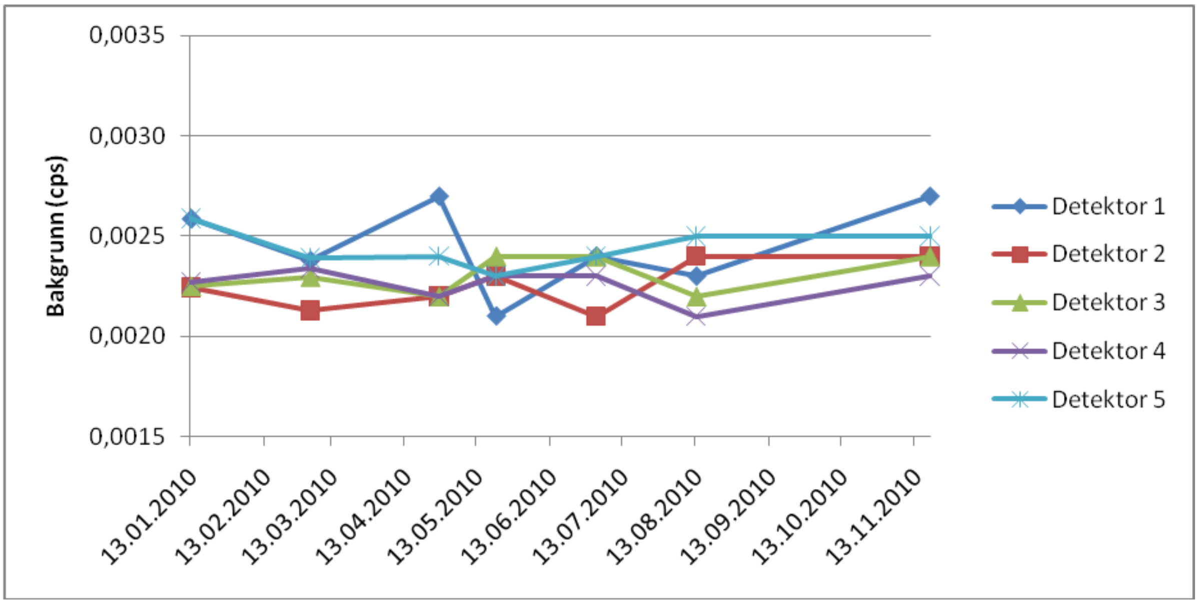


Figure 2.12: Background count rate (cps) in 2010. Repeated measurements of filter blanks for each of the five detectors.

More information on the statistics of counting is given in Appendix 6.

2.2.4 Calculation of results

Chemical yield

At the beginning of the analysis, a known amount of Re (8.00 mg) is added as a yield monitor to each sample. At the end of the analysis, Re (and ^{99}Tc) is precipitated as a tetraphenyl arsonium salt, $(C_6H_5)_4AsReO_4$. The mass of $(C_6H_5)_4AsReO_4$ is determined and the chemical yield is calculated from the percentage recovery of rhenium. It is assumed that the ^{99}Tc present is not contributing significantly to the mass of the precipitate. The atomic mass of Re and the molar mass of $(C_6H_5)_4AsReO_4$, is given in table 2.4. Box 2.1 shows an example of calculation of chemical yield for a sample.

We have that 1 mole of Re corresponds to 1 mole of $(C_6H_5)_4AsReO_4$.

The percentage recovery (U %) is given by

$$U\% = \frac{Massof\,(C_6H_5)_4\,As\mathrm{Re}O_4(g)\cdot 186.207g/mol}{Massof\ \mathrm{Re}added(g)\cdot 633.548g/mol}\cdot 100\%$$

Table 2.4: Atomic mass of Re, mass of Re added and the molar mass of tetraphenyl arsonium perrhenat

		Molar mass (g/mol)	**Atomic mass (g/mol)**	**Mass (g)**
Rhenium	Re		186.207	0.00800 ± 0.00001
Tetraphenyl arsonium perrhenate	$(C_6H_5)_4AsReO_4$	633.548		

Box 2.1: Example of calculation of chemical yield for the sample from station T10

Sample ID: JH050710 st 498 (T10)

Mass of precipitate, $(C_6H_5)_4AsReO_4$, m = 0.0204 g

Percentage yield: $U\% = \frac{0.0204g \cdot 186.207 g/mol}{8.00 \cdot 10^{-3} g \cdot 633.548} \cdot 100\% = 75\%$

The chemical yields for the samples analysed in this study were in the range 58 – 95 %, with a mean of 80 ± 8 % (1 SD). (see Appendix 4: Excel sheet with calculation of results). The most likely explanation for the relatively low yield of 58 % for the sample collected at station 11 (576), is that a part of the sample ran outside of the filter paper and some of the precipitate laid on top of the BioRad resin during the anion exchange step described in section 2.2.1.

Activity concentration of ^{99}Tc

The activity concentration of ^{99}Tc in a sample in mBq L^{-1} is given as[6]

$$^{99}Tc - concentration = \left[cps - \overline{cps}(filterblanks)\right] \cdot \frac{100}{U\%} \cdot \frac{100}{E\%} \cdot \frac{1000}{V(L)}$$

Where

cps = counts per second (of the sample)

$\overline{cps}(filterblanks)$ = the mean value of the last 12 counts of filter blanks (counts per second, cps)

U% = the percentage recovery

E% = the counting efficiency for ^{99}Tc (efficiency as a function of source weight, given in efficiency tables for each of the five detectors) (E = cps Bq^{-1})

V = volume of the sample given in litres

The information provided by the detector is the number of counts that the instrument is able to register. By dividing the number of counts with the time interval, t, the counts per minute (cpm) or counts per second (cps) is obtained. In order to calculate the activity (i.e.

---

[6] mBq L^{-1} = Bq m^{-3}

disintegrations per time unit; disintegrations per minute (dpm) or disintegrations per second (dps=Bq), the efficiency (e) of the detector has to be taken into account.

The activity (in Bq) of a radioactive sample is thus given by:

dps (disintegrations per second)=Bq (Becquerel) = cps/e

cps is given with four decimals, and the results are calculated using a Microsoft Office Excel work sheet, where all decimals are taken into account. A copy of the Excel sheet with calculation of results is given in Appendix 4.

2.2.5 Precision of analysis

The two main sources of errors in the method are associated with the gravimetric determination of chemical yield and counting statistics.

It is assumed that a standard error of ± 5 % covers the uncertainties of the gravimetric yield determination. This analytical error includes the collective uncertainties of the gravimetric procedure, such as calibration of the detector, the determination of mass of the final precipitate and the physical characterisation of the final source.

For the beta counting we have:

$$\%\sigma_{S-B} = \frac{100}{S-B}\sqrt{\frac{S}{t_s}+\frac{B}{t_b}}$$

where

% σ_{S-B} = the percent standard deviation of the net count-rate of the sample $\left\lfloor cps - \overline{cps}(filterblanks)\right\rfloor$

S = sample count-rate (counts per second, cps)

B = background count-rate, $\overline{cps}(filterblanks)$ = the mean value of the last 12 counts of filter blanks (counts per second, cps)

t_s = the counting time of the sample in seconds (normally 172800 seconds)

t_b = the counting time of filter blanks in seconds (always 172800 secounds)

The total percent uncertainty in the analysis is given by:

$$\text{Total uncertainty } (\%) = \sqrt{\left(\frac{100\sqrt{\left(\frac{S}{t_s}+\frac{B}{t_b}\right)}}{S-B}\right)^2 + (5)^2}$$

In all samples from 2010 analysed during this master project, the relative analytical error due to the combined uncertainty in the chemical yield and the counting statistics were generally between 5 and 10 %, which is normal for this analysis.

2.2.6 Lower limit of detection

The lower limit of detection (LLD) is calculated in accordance with the EML Procedures Manual, HASL-300 (EML, 1997). It is assumed that the number of counts is sufficient for the Poisson distribution to approach the Gaussian distribution so that Gaussian statistics can be used.

The LLD has been defined as *"the smallest amount of sample activity that will yield a net count for which there is a confidence at a predetermined level that activity is present."* (Pasternack and Haley, 1971, in (EML, 1997) Section 4.5.3. page 5).

The lower limit of detection at the 95 % confidence level is given by:

$LLD_{95\%} = (k_\alpha + k_\beta)\ S_s = 3.29\ S_s$

where

k_α = the upper percentile of the standard normal distribution corresponding to the preselected risk for concluding falsely that activity is present. At the 95 % confidence level $\alpha = 0.05$, and $k_\alpha = 1.645$

k_β = the corresponding value for the predetermined degree of confidence for detecting the presence of activity $(1 - \beta)$. At the 95 % confidence level $(1 - \beta) = 0.95$, and $k_\beta = 1.645$

Thus, at $LLD_{95\%}$, $k_\alpha + k_\beta = 1.645 + 1.645 = 3.29$

S_s = the standard error in the sample

The standard error, S_s is given by:

$$S_s = \sqrt{\left(S_{gross} + \left(S_{Bk}\right)^2\right)}$$

where

S_{gross} = the mean background counts

S_{Bk} = the standard deviation in S_{gross}

In 2009, the background values was

$S_{gross} = (0.002425\ \text{cps} \cdot 172800\ \text{sec}) = 419$ counts

$S_{Bk} = (0.000197\ \text{cps} \cdot 172800\ \text{sec}) = 34$ counts

This gives us:

$$S_s = \sqrt{\left(419 + 34^2\right)} = 40$$

The $LLD_{95\%}$ must be converted to activity (Bq):

$$LLD_{95\%}(Bq) = \frac{3.29 S_S}{t_s \cdot E \cdot U}$$

where

t_s = the counting time of the sample in seconds (normally 172800 seconds)

E = the mean counting efficiency of the measurement system (cps Bq^{-1})

U = the average chemical yield

For the ^{99}Tc method of analysis, we have:

t_s = 172800 seconds

E = 0.22 cps Bq^{-1} (average mean counting efficiency for 2009)

U = 0.72 (average chemical yield for 2009)

$$LLD_{95\%}(Bq) = \frac{3.29 \cdot 40}{172800 \cdot 0.22 \cdot 0.72} = 0.0048 Bq$$

The theoretical lower limit of detection for 100 L of seawater is thus 0.05 Bq m^{-3}:

$$\frac{0.0048 Bq}{100 L} = 0.000048 \frac{Bq}{L} = 0.05 \frac{mBq}{L}$$

2.2.7 Quality assurance

Intercomparison exercise ^{99}Tc in seawater samples from the North Sea 2010

Two additional surface seawater samples were collected from two stations; T9 (in the NwCC) and 30 (in the central North Sea), in order to perform an intercomparison exercise. The samples were sent to CEFAS and analysed for ^{99}Tc by CEFAS personnel. The results from this intercomparison exercise are shown in table 2.5 and figure 2.13. The IMR ^{99}Tc result for station T9 was 0.40 ± 0.03 Bq m^{-3}, while CEFAS reported a value of 0.25 ± 0.06 Bq m^{-3}. For station 30 the IMR result was 0.43 ± 0.03 Bq m^{-3} and the CEFAS result was 0.25 ± 0.06 Bq m^{-3}. The mean for the results of the analyses of samples from station T9 and 30 were 0.33 and 0.34 Bq m^{-3}, respectively.

The IMR and CEFAS ^{99}Tc results differed with about 40 % for both station T9 and station 30. This is a rather large discrepancy. CEFAS and IMR both use the analytical method based upon Harvey et al. (1992). While the IMR samples were pre-treated aboard the ship and analysed short time after sampling, the seawater samples sent to CEFAS were stored in polyethylene carboys (not added yield monitor aboard the ship) and analysed in February/March 2011. For radionuclides other than ^{99}Tc, storage effects such as adsorption onto container walls could have been a source of error. But adsorption of ^{99}Tc onto walls is considered unlikely. If, however, there were large amounts of algae in the water, adsorption of ^{99}Tc onto this could have occurred. However, little algae were observed and this is also considered unlikely.

Another possible, but rather unlikely explanation, is that rhenium could have precipitated out of the solution under cold conditions aboard the ship (unlikely in July). If this, nevertheless, was the case, the concentration of the Re-yield monitor was less than 4 mg Re/ml, and the IMR samples were underspiked, giving an overestimate of the result. It can be mentioned that CEFAS uses a Re-standard concentration of 5 mg Re/ml, while IMR uses 4 mg Re/ml. This should in principle not affect the results.

Other possible reasons for the different results could be sources of error in the analytical procedure, such as loss of ^{99}Tc during dry ashing, wrong concentration of the yield monitor (Re-standard) or calibration of the detector.

Table 2.5: Results from the intercomparison exercise: ^{99}Tc (Bq m^{-3}) in surface seawater samples from station T9 and 30 in the North Sea in 2010. Uncertainty of the mean is given as deviation from the mean value.

Sample ID	**IMR result** ^{99}**Tc (Bq m^{-3})**	**CEFAS result** ^{99}**Tc (Bq m^{-3})**	**Mean** ^{99}**Tc (Bq m^{-3})**
CTD 503 St T9	0.40±0.03	0.25±0.06	0.33±0.08
CTD 516 St 30	0.43±0.03	0.25±0.06	0.34±0.09

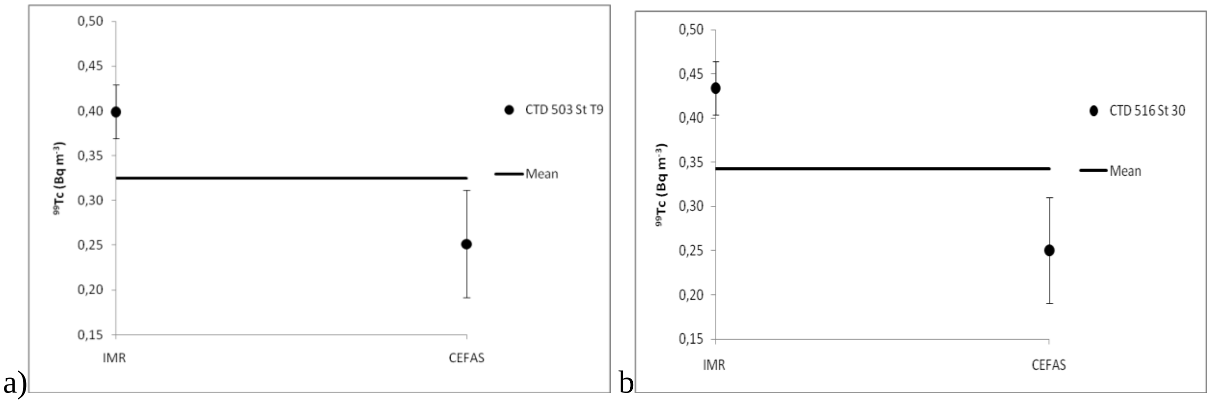


Figure 2.13: ^{99}Tc (Bq m^{-3}) in seawater intercomparison between IMR and CEFAS. a) station T9 and b) station 30. The solid line represent the mean.

It should, however, be mentioned that IMR have participated in several international laboratory intercomparison exercises where the analytical results have been good. For example, in 2006 IMR participated in a small intercomparison with respect to levels of ^{99}Tc in a homogenized seawater sample. The intercomparison exercise was organised by NRPA, and six laboratories participated. The mean value was 0.55±0.11 Bq m^{-3}, and the reported IMR result was 0.54 ± 0.03 Bq m^{-3} (letter from Mark Dowdall (senior scientist NRPA), dated 18.10.2006, addressed to H.E. Heldal, IMR).

Quality control

Table 2.6 and figure 2.14 shows the results from replicate analysis of the ”quality-control” (QC) sample prepared from Fucus seaweed. The average chemical yield was 91.1 ± 3.1 % and the average ^{99}Tc activity concentration was 1.22 ± 0.09 Bq ml^{-1}. All concentrations were within 2 estimated standard deviations (±2SD) from the mean. This indicates that good reproducibility has been obtained with the QC during the analyses. However, it is important to notice that only 4 measurements is to few to give a good estimate of the standard deviation.

Table 2.6: Chemical yield (%) and ^{99}Tc activity concentrations in quality control samples analysed during the master project

Sample ID	Chemical yield (%)	^{99}Tc activity concentration (Bq ml^{-1})
QC 070510	93.38	1.31
QC 160810	87.13	1.28
QC 240810	93.75	1.15
QC 130910	90.07	1.14
Mean ± 1 SD	*91.1 ± 3.1*	*1.22 ± 0.09*

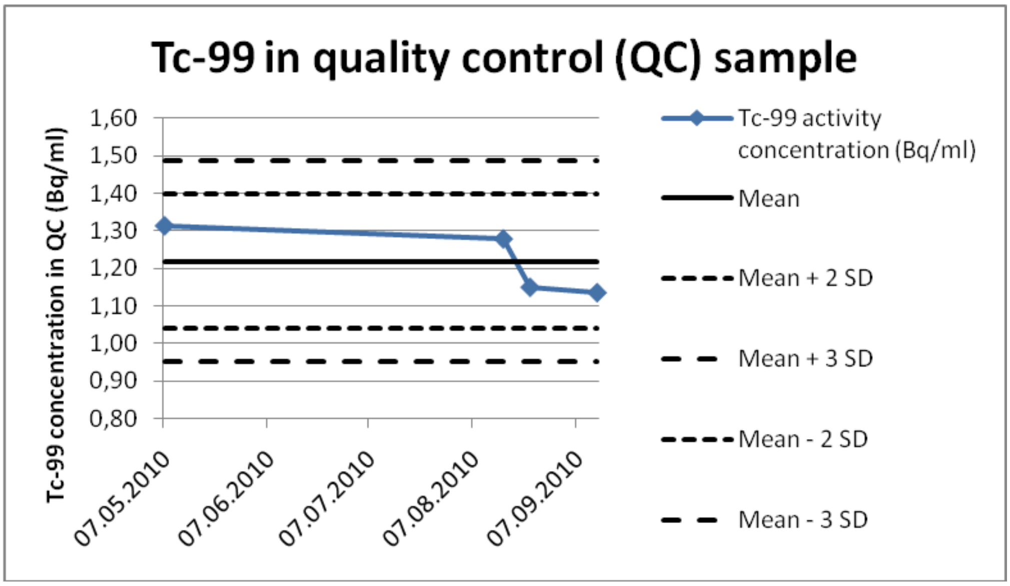


Figure 2.14: Measurements of ^{99}Tc in the quality control sample during the master project

2.3 Samples collected before 2010

Historical data from ^{99}Tc measurements of seawater samples collected in the period 1998-2009 have also been used in this master project. The sampling locations for collection of seawater samples during the years 2003-2010 are shown in figure 2.15. In order to get familiar with the ^{99}Tc-method, analyses of seawater samples collected in 2008 and 2009 were performed during the autumn 2009 and spring 2010. A brief description of the sample collection and analyses of the historical samples is given below.

Samples collected in the period 1998-2000

The samples collected in the period 1998-2000 were collected on board IMR's vessels and pre-treated on board by H. E. Heldal. The sample collection was performed as described in chapter 2.1.3 (H. E. Heldal, pers. comm.). The Tc-columns were thereafter sent to CEFAS, where they were analysed by CEFAS personnel using the method described by Harvey et al. (1991, 1992). A description of the collection and analyses of these samples are also given in (Heldal, 2001, Karcher et al., 2004, Kershaw et al., 2004).

Samples collected in the period 2003-2006

The samples collected in the period 2003-2006 were collected within the RADNOR program (Heldal et al., 2007a, Heldal et al., 2007b) along the Norwegian shoreline by local fishermen or H. E. Heldal (H. E. Heldal, pers. comm.). The samples were sent unprocessed to IMR, where they were pre-treated prior to analysis.

All the samples were analysed at IMR using the method described in chapter 2.2 (H. E. Heldal, pers. comm.). The method used is described in detail in (Heldal, 2009, Heldal and Sjøtun, 2010), and is a modified version of the method described by Harvey et al. (1991, 1992).

Samples collected in the period 2006-2009

The samples collected in the period 2006-2009 were collected within the RAME program (see chapter 1.5) on board IMR's vessels by different cruise participants (H. E. Heldal, pers. comm.). Some of the samples were pre-treated on board the vessels by the different cruise participants, and some of the samples were sent unprocessed to IMR. The unprocessed samples were pre-treated at IMR prior to analysis.

All the samples were analysed at IMR using the method described in chapter 2.2 (H. E. Heldal, pers. comm.). The method used is described in detail in Heldal (2009), and is a modified version of the method described by Harvey et al. (1991, 1992). Some samples collected in 2008 and 2009 (from the Barents Sea) were analysed during this master project under supervision from H. E. Heldal. A description of the collection and analyses of these samples are also given in (NRPA, 2008, NRPA, 2009, NRPA, 2011).

In Appendix 5 the 23 samples collected in 2008 (from the Barents Sea) and 12 samples from 2009 (from the Barents Sea) that were analysed during this master project are marked with an X.

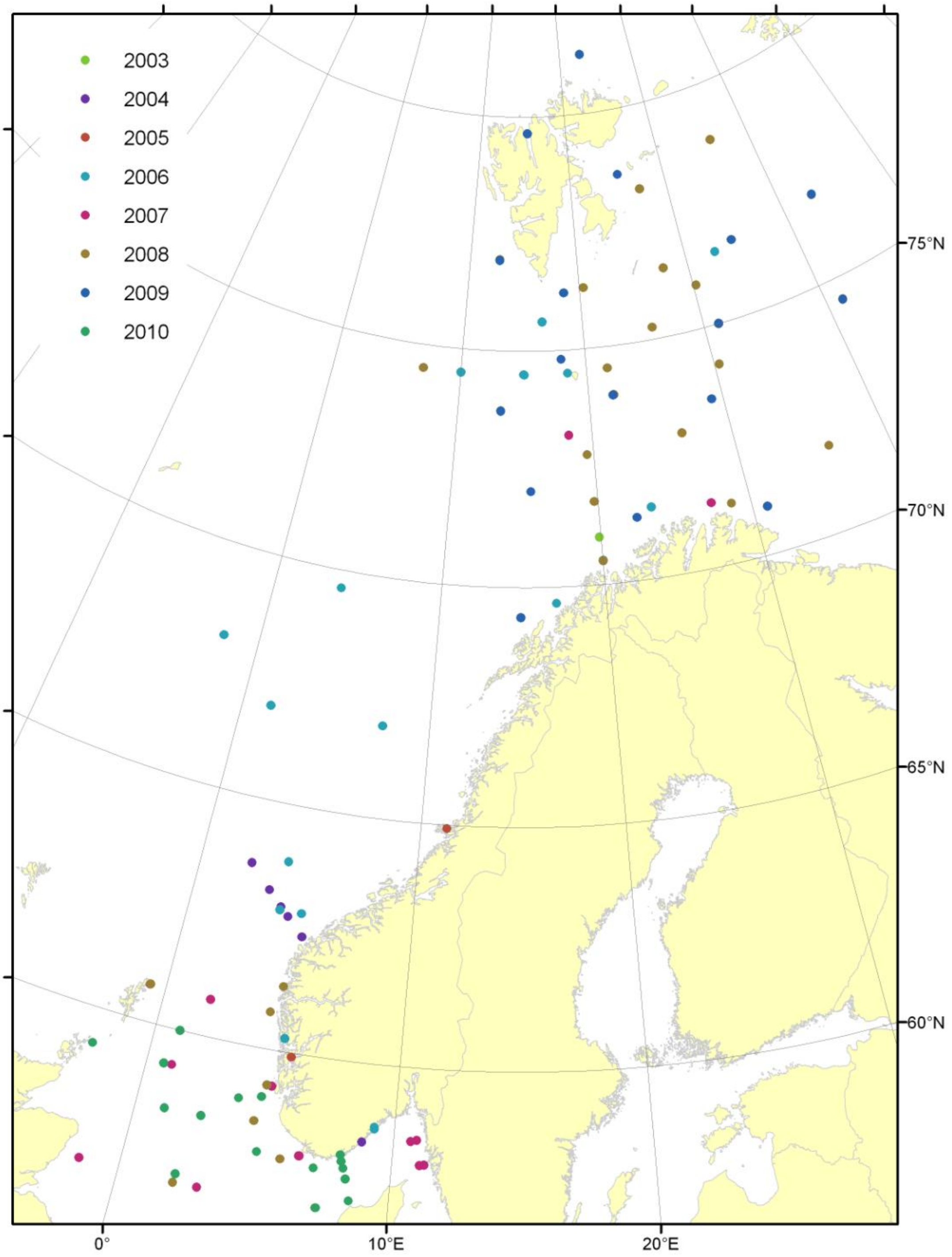


Figure 2.15 Sampling stations for collection of surface water during the years 2003-2010.

In the present study, no statistical tests were performed, due to the relatively limited data set.

3. Results

In this chapter, the 2010 results are presented first, in order to give a picture of the present ^{99}Tc levels in the North Sea and Skagerrak (3.1). Thereafter, the historical ^{99}Tc data from IMR and time-series of ^{99}Tc in the North and Nordic Seas in the period 1998 to 2010 are presented in chapter 3.2 and 3.3. At the end of the chapter, the results from measurements of ^{99}Tc at the fixed coastal station Værlandet are presented.

3.1 ^{99}Tc, salinity and temperature in seawater from the North Sea in 2010

The ^{99}Tc activity concentrations in the 20 seawater samples collected during the cruise with R/V Johan Hjort in the North Sea and Skagerrak in July/August 2010 are presented in table 3.1. The spatial distribution is shown in figure 3.1. The activity concentrations ranged from 0.12±0.01 to 0.77±0.04 Bq m^{-3}, with an overall mean value of 0.33 ± 0.14 Bq m^{-3} (the uncertainty in the mean is the standard deviation of the dataset). All activity concentrations were significantly above the detection limit (0.05 Bq m^{-3}).

The salinity and temperature are also presented in Table 3.1. The salinities ranged from below 30 in the Skagerrak water to above 35 in the Atlantic water mass in the northern North Sea. The sea surface temperatures ranged from 11.3 to 16.4 °C, with the maximum temperatures in the Skagerrak (~14-16°C), and lower temperatures (~12-14°C) in the water masses in the North Sea with higher influence of Atlantic water. In the NwCC the temperatures ranged from 11-15°C.

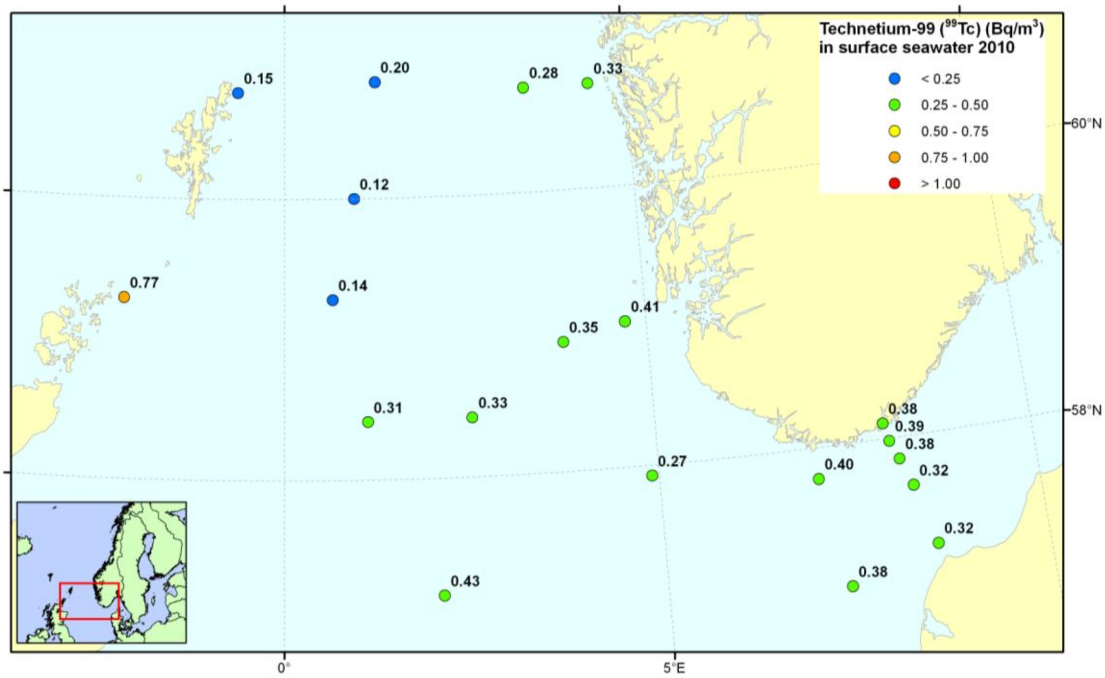


Figure 3.1: The spatial distribution of ^{99}Tc in surface water of the North Sea and the Skagerrak in July/August 2010.

Table 3.1: Activity concentrations of ^{99}Tc (Bq m^{-3}) in surface seawater samples collected in the North Sea and Skagerrak during the cruise with R/V 'Johan Hjort' in July /August 2010, including sampling dates, sampling locations, depths (m), salinity (psu) and temperature (°C). The error includes a statistical counting error and uncertainties in the chemical procedure, see chapter 2.2.5. NwCC=Norwegian Coastal Current, ECB=East Coat of Britain, nm=not measured. The colours in the table correspond to figure 3.1; blue: < 0.25 Bq m^{-3}, green: 0.25-0.50 Bq m^{-3}, orange: 0.75-1.00 Bq m^{-3}.

Station	**Area**	**Sampling date**	**Latitude**	**Longitude**	**Depth (m)**	**Sampling depth (m)**	**Salinity (psu)**	**Temperature (°C)**	**^{99}Tc (Bq m^{-3})**
T10	NwCC	05.07.2010	59° 02.0' N	4° 42.65' E	276	5	34.155	11.3	0.41±0.0.3
T9	NwCC	06.07.2010	57° 46.85' N	7° 5.93' E	400	5	31.515	13.0	0.40±0.03
22	Skagerrak	07.07.2010	57° 58.87' N	8° 5.68' E	466	5	29.040	15.5	0.39±0.02
19	Skagerrak	07.07.2010	58° 6.56' N	8° 2.26' E	210	5	30.204	13.8	0.38±0.02
26	Skagerrak	08.07.2010	57° 50.85' N	8° 11.82' E	526	5	28.938	15.8	0.38±0.02
28	Skagerrak	08.07.2010	57° 39.0' N	8° 19.81' E	219	5	29.448	16.4	0.32±0.02
X	Skagerrak	08.07.2010	57° 13.12' N	8° 32.58' E	nm	5	31.36	15.8	0.32±0.02
29	North Sea	08.07.2010	56° 59.96' N	7° 21.82' E	42	5	32.957	14.8	0.38±0.02
30	North Sea	10.07.2010	57° 10.26' N	2° 5.15' E	84	5	35.047	13.8	0.43±0.03
T26	NwCC	13.07.2010	57° 55.56' N	4° 54.19' E	101	5	34.387	13.6	0.27±0.02
13	North Sea	15.07.2010	58° 25.23' N	2° 32.9' E	72	5	35.050	13.9	0.33±0.02
14	North Sea	17.07.2010	58° 24.64' N	1° 8.03' E	138	5	35.145	13.6	0.31±0.02
T11	NwCC	18.07.2010	58° 55.19' N	3° 50.5' E	276	5	33.952	13.4	0.35±0.02
11	North Sea	19.07.2010	59° 16.9' N	0° 40.38' E	136	5	35.231	13.3	0.14±0.02
10	North Sea/ECB	19.07.2010	59° 17.0' N	2° 13.84' W	98	5	34.722	11.8	0.77±0.04
6	North Sea	26.07.2010	60° 0.02' N	0° 59.73' E	123	5	35.114	13.9	0.12±0.01
3	NwCC	27.07.2010	60° 44.99' N	3° 30.3' E	323	5	33.231	14.5	0.28±0.02
T27	North Sea	29.07.2010	60° 50.0' N	1° 19.73' E	142	5	34.813	13.7	0.20±0.02
1	North Sea	31.07.2010	60° 45.56' N	0° 40.67' W	109	5	35.244	12.4	0.15±0.01
4	NwCC	01.08.2010	60° 44.96' N	4° 27.08' E	372	5	31.308	14.7	0.33±0.02

3.1.1 Spatial distribution of ^{99}Tc in surface seawater

The maximum ^{99}Tc activity concentration (0.77±0.04 Bq m^{-3}) was observed in the sample collected at station 10, off the east coast of Scotland (Orkney Islands) (Figure 3.1). This sampling location was the one located furthest to the west, in the area where seawater containing radionuclides from Sellafield enters the North Sea. The lowest ^{99}Tc activity concentrations were observed in samples collected in the north- western part of the North Sea at station 6, 11, 1 and T27 (range 0.12±0.01 – 0.20±0.02 Bq m^{-3}). The lowest activity concentrations were found in saline Atlantic water (salinity > 35), a water mass low in Sellafield radionuclides. Further south in the northern North Sea the activity concentrations were noticeable higher (range 0.31±0.02 - 0.43±0.03 Bq m^{-3}) with the concentration at station 30 (0.43±0.03 Bq m^{-3}) as the second highest observed. Station 30 was the station furthest south on the cruise route, and could be allocated to the central North Sea. The overall mean ^{99}Tc activity concentration in the northern part of the North Sea, (referred to as “the North Sea” in figures and tables) was 0.26 ± 0.12 Bq m^{-3} (the uncertainty in the mean is the standard deviation of the dataset).

In the five samples taken in the Skagerrak, ^{99}Tc activity concentrations were quite uniform; range from 0.32±0.02 to 0.39±0.02 Bq m^{-3} with a mean value of 0.35 ± 0.03 Bq m^{-3}. The highest activity concentrations in this area were observed in the Skagerrak coastal water, having low salinity (<30) and relatively high temperature. The temperatures in the Skagerrak water ranged from 13.8 to 16.4 °C, and were the highest encountered during the cruise.

In the Norwegian Coastal Current the activity concentrations of ^{99}Tc ranged from 0.27±0.02 to 0.41±0.03 Bq m^{-3}, with a mean value of 0.34 ± 0.06 Bq m^{-3}. Thus, the levels in the NwCC were a factor of 2 higher than the levels observed in the north-western part of the North Sea, and a factor of 2 lower than the activity concentration observed off the Scottish coast. The salinity in the NwCC samples ranged from 31.3 to 34.4.

3.1.2 Variation of ^{99}Tc activity concentration with respect to salinity

In Figure 3.2, ^{99}Tc activity concentrations (Bq m^{-3}) in surface waters of the North Sea and Skagerrak in July/August 2010 are plotted against salinity. Although the figure does not show a strong correlation between salinity and ^{99}Tc activity concentration, it can be seen that samples from the northern North Sea with high influence of open Atlantic water (high salinity) have the lowest ^{99}Tc activity concentrations. The data point with relatively high salinity and high activity concentration is the sample from station 10 off the east coast of Scotland.

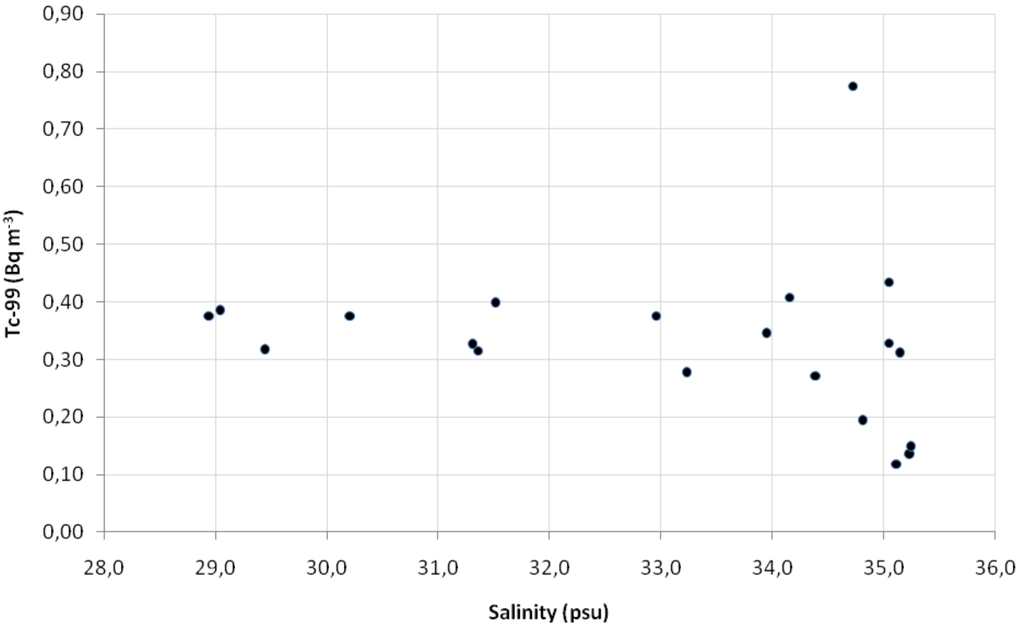


Figure 3.2: Activity concentrations of ^{99}Tc (Bq m^{-3}) vs. salinity in surface seawater of the North Sea in 2010. The degree of variability in the ^{99}Tc activity concentrations is low for samples with salinities between 29 and 34, and somewhat higher for samples with salinities above 34.

3.2 Historical ^{99}Tc data from IMR

The results of all ^{99}Tc determinations carried out by IMR on seawater samples collected during the years 1998 – 2010 are given in Appendix 5. In the appendix, bottom samples and samples collected from the water column are also included, in addition to surface seawater samples. No samples were collected by IMR in 2001 and 2002. Distribution maps showing the activity concentrations of ^{99}Tc in surface water samples collected in the North and Nordic Seas during the years 1998-2010 are presented in figures 3.3-3.11.

1998-2000

During 1998, 1999 and 2000, samples from the Norwegian Sea, Greenland Sea and NwCC north of Stad were collected by IMR and analysed for ^{99}Tc at CEFAS (The Centre for Environment, Fisheries & Aquaculture Science). The results have been reported in Kershaw et al. (2004) and are presented in figure 3.3. In 1998, the ^{99}Tc activity concentrations in the Norwegian Sea ranged from below detection limit (<0.04 Bq m^{-3}) to 0.86±0.04 Bq m^{-3}. The highest activity concentration was observed within the NwCC. In 1999 the levels in the Norwegian Sea, Greenland Sea and NwCC ranged from 0.09±0.02 Bq m^{-3} to 1.61±0.07 Bq m^{-3}. Low levels were observed in the Greenland and Norwegian Sea and elevated levels in the NwCC. Similar levels were observed in 2000, with ^{99}Tc activity concentrations in the Norwegian/Greenland Sea ranging from 0.05±0.01 to 0.39±0.02 Bq m^{-3} and 0.63±0.03 – 1.19±0.05 Bq m^{-3} in the NwCC.

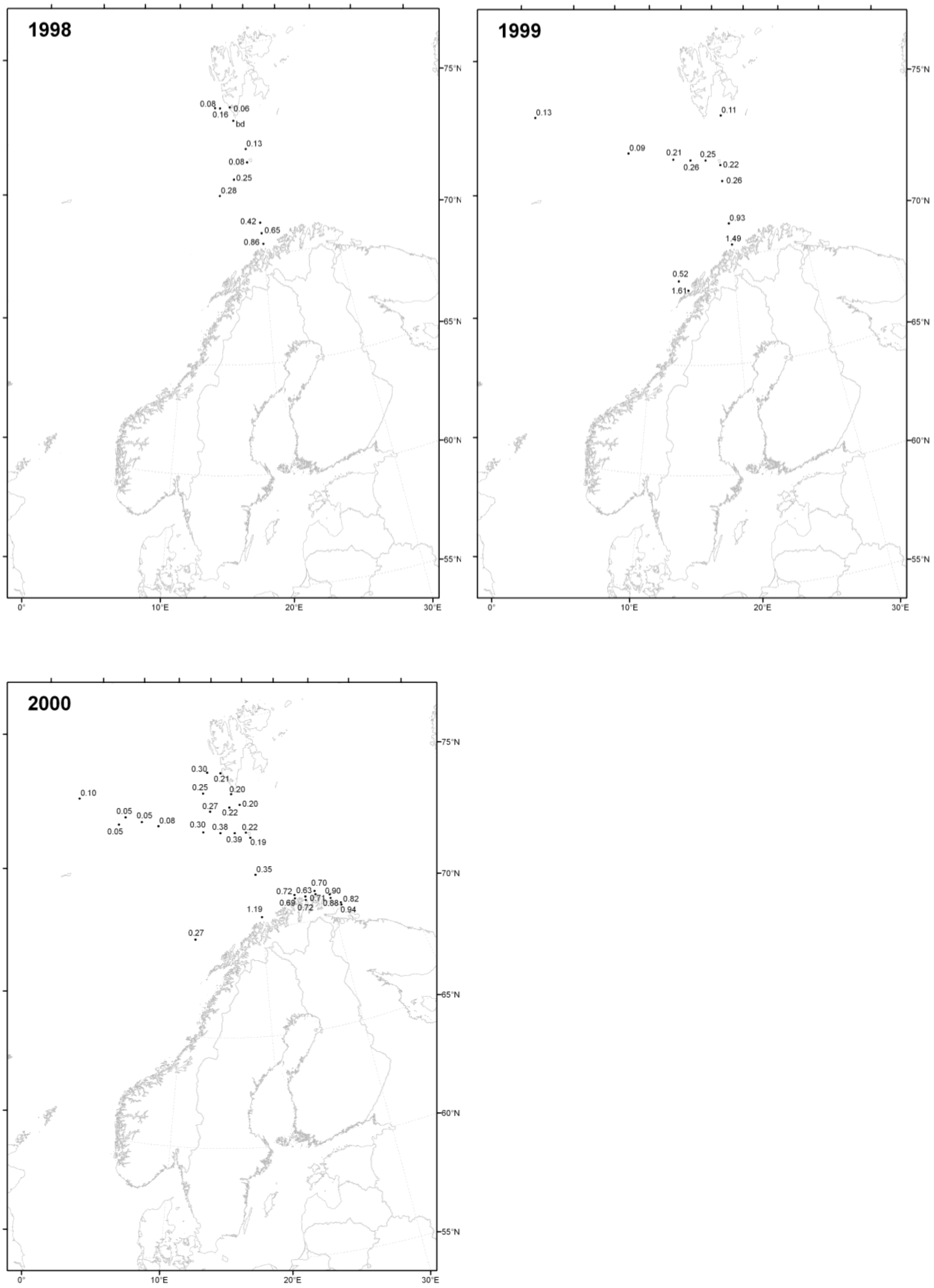


Figure 3.3: Distribution maps showing activity concentrations of ^{99}Tc (Bq m^{-3}) in surface seawater samples collected during 1998, 1999 and 2000. The data have been reported in Kershaw et al. (2004).

2003

In 2003, a total of 7 surface seawater samples were collected and analysed for ^{99}Tc, and the results are presented in figure 3.4. The results of the samples from Arendal, Værlandet and Rørvik have been published in Heldal et al. (2007). The results of the two samples taken in the northern part of the NwCC and one sample collected in the Norwegian Sea are unpublished data from H.E. Heldal (pers. comm.). The seawater sample collected at the station near Arendal in Skagerrak had a relatively low ^{99}Tc activity concentration of 0.39±0.02 Bq m^{-3}. The highest level, 1.01±0.05 Bq m^{-3}, was measured in the NwCC south of Stad, in a sample collected at Værlandet in western Norway in May 2003. In December, the activity concentration at Værlandet had decreased to 0.70 Bq m^{-3}. The sample collected at the sampling location outside Rørvik in mid-Norway had a ^{99}Tc activity concentration of 0.74±0.04 Bq m^{-3}. Further northwards in the NwCC, on the Fugløya-Bear Island transect, the activity concentrations were lower (0.50±0.02 Bq m^{-3} and 0.36±0.02 Bq m^{-3}). In the only surface sample from the Norwegian Sea that year, the ^{99}Tc activity concentration was 0.08±0.01 Bq m^{-3}, which is very low and close to the detection limit.

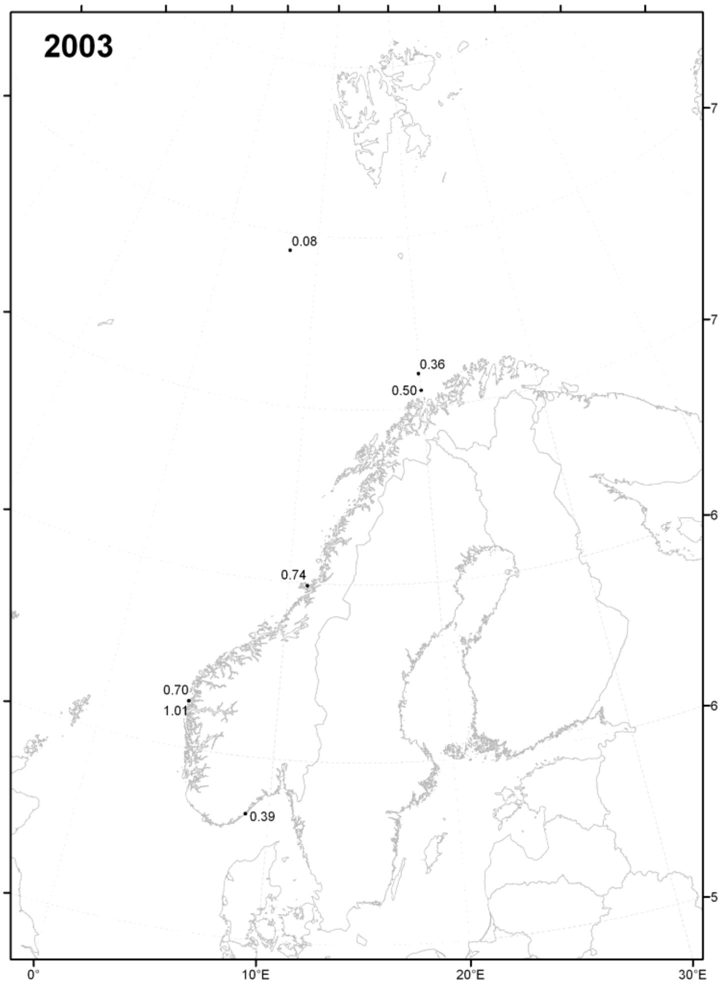


Figure 3.4: Distribution map showing activity concentrations of ^{99}Tc (Bq m^{-3}) in surface seawater samples collected during 2003. The data from Arendal, Værlandet and Rørvik have been reported in Heldal et al. (2007). The three northern samples are not reported previously.

2004

In 2004, a total of 8 surface samples of seawater were collected and analysed for ^{99}Tc. The results are presented in figure 3.5. The results from the three samples collected along the southern coast of Norway; Arendal, Tysnes and Værlandet have been reported by Heldal et al (2007). In the sample collected in Skagerrak (Arendal) the ^{99}Tc activity concentration was 1.03±0.05 Bq m^{-3}, which is almost three times higher than the level observed in 2003. The ^{99}Tc activity concentrations at Tysnes and Værlandet in western Norway were almost identical, 0.77±0.04 and 0.76±0.03 Bq m^{-3}, respectively. The five northern samples were taken on a transect out in the southern part of the Norwegian Sea (the Svinøy section), with the two samples collected in the NwCC having ^{99}Tc activity concentrations of 1.32±0.06 Bq m^{-3} and 1.33±0.06 Bq m^{-3}, and the three samples collected in the Norwegian Sea having considerably lower ^{99}Tc levels (range 0.05±0.01 to 0.12±0.01 Bq m^{-3}) (Heldal, unpublished data).

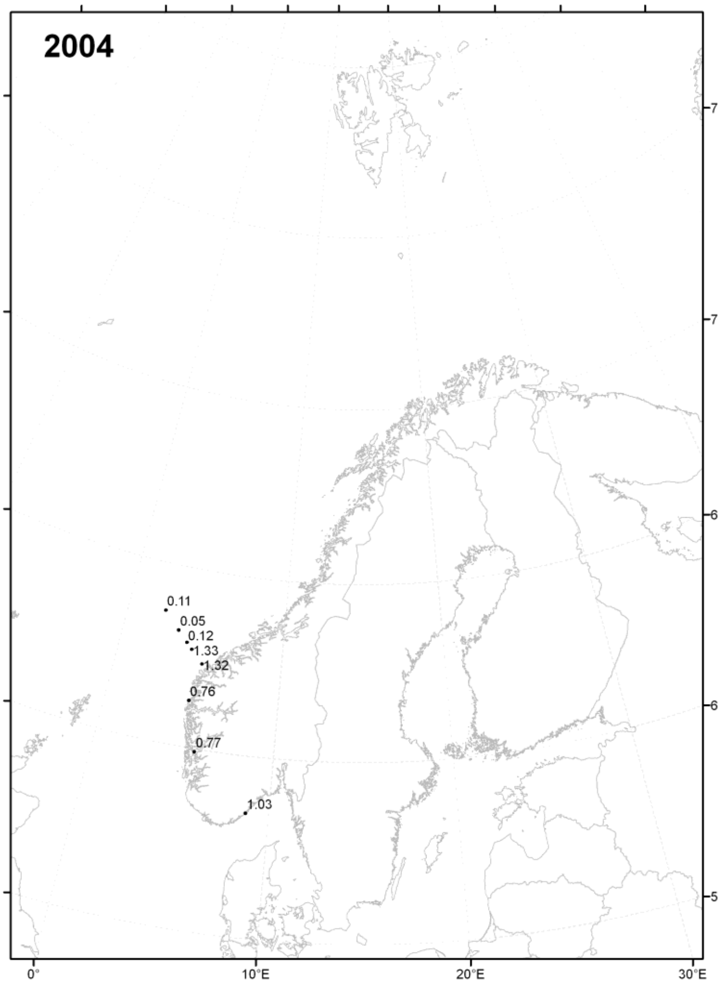


Figure 3.5: Distribution map showing activity concentrations of ^{99}Tc (Bq m^{-3}) in surface seawater samples collected during 2004. The data from Arendal, Tysnes and Værlandet have been reported in Heldal et al. (2007), while the other data are not previously reported.

2005

In 2005, a total of 10 surface seawater samples were collected. Two samples were analysed short time after sampling (Tysnes and Rørvik, reported in Heldal et al. (2007), while the rest of the samples have been stored in the refrigerator at the isotope laboratory at IMR and were analysed in 2010/2011 by H.E. Heldal. The results are presented in figure 3.6. The ^{99}Tc activity concentrations in the North Sea ranged from 0.80±0.05 to 1.92±0.10 Bq m^{-3}, and the highest values were measured in the central and eastern part of the North Sea (1.92 and 1.90 Bq m^{-3}, respectively). In the sample collected on the border between Skagerrak and Kattegat, the activity concentration was relatively low, 0.76±0.05 Bq m^{-3}. In the NwCC, a gradual decrease in activity concentrations was observed, from 1.05±0.06 Bq m^{-3} in the southern part to 0.69±0.03 Bq m^{-3} in the sample from Rørvik. The ^{99}Tc activity concentration in the sample from Tysnes was 0.87±0.04 Bq m^{-3}.

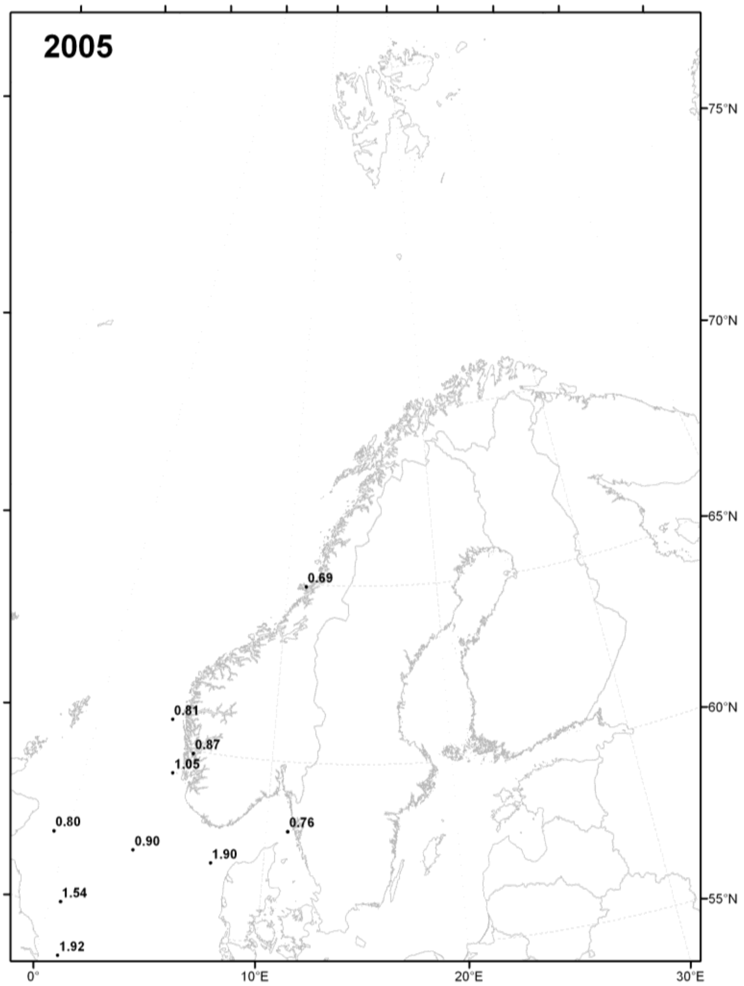


Figure 3.6: Distribution map showing activity concentrations of ^{99}Tc (Bq m^{-3}) in surface seawater samples collected during 2005. The data from Tysnes and Rørvik have been reported in Heldal et al. (2007), while the other data are not previously reported.

2006

During 2006, 28 surface seawater samples were collected in the Norwegian Sea, the Barents Sea and along the Norwegian coast and analysed for ^{99}Tc at IMR. The results are presented in figure 3.7 and table 3.2 (Espegrend). In Figure 3.7 the average value for Espegrend (0.71) is shown. The results in figure 7 have been published in NRPA (2008) and the results in table 3.2 have been published by Heldal and Sjøtun (2010). One sample from the Norwegian Sea had a ^{99}Tc activity concentration below the detection limit (<0.04 Bq m^{-3}). Omitting the result below the detection limit, the activity concentrations of ^{99}Tc in surface water in the Norwegian Sea ranged from 0.07±0.01 Bq m^{-3} in open waters to 0.80±0.04 Bq m^{-3} in the

NwCC. In the Barents Sea the activity concentration of ^{99}Tc ranged from 0.09±0.01 to 0.18±0.01 Bq m^{-3}. The results from the two samples collected in the Skagerrak, at the coastal stations Truslvik and Randvika, were 0.47±0.03 and 0.63±0.04 Bq m^{-3}, respectively. The sample from Værlandet has an activity concentration of 0.62±0.03 Bq m^{-3}, slightly lower than the levels observed in 2003 and 2004.

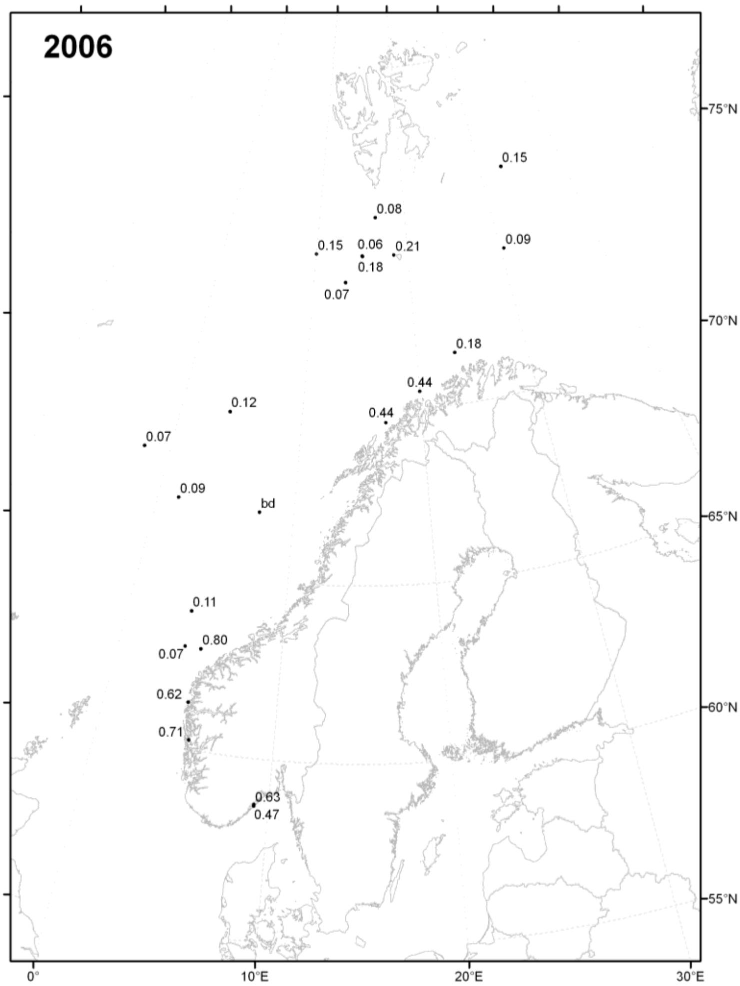


Figure 3.7: Distribution map showing activity concentrations of ^{99}Tc (Bq m^{-3}) in surface seawater samples collected during 2006. The data have been reported in NRPA (2008), except for the activity concentration south of Bergen (0.71), which is an average of 7 measurements of samples taken between February and December 2006; see Table 3.2)

Table 3.2: Sampling dates, salinities and activity concentrations of ^{99}Tc in surface seawater collected at Espegrend in 2006. nm=not measured.

Sampling date	Salinity	^{99}Tc (Bq m^{-3})	Reference
26.01.2006	32.4190	1.01±0.06	(Heldal and Sjøtun, 2010)
22.02.2006	32.3595	0.75±0.04	(Heldal and Sjøtun, 2010)
20.04.2006	29.9360	0.67±0.04	(Heldal and Sjøtun, 2010)
19.06.2006	32.4170	0.67±0.04	(Heldal and Sjøtun, 2010)
31.08.2006	29.9865	0.54±0.03	(Heldal and Sjøtun, 2010)
16.11.2006	29.5475	0.62±0.04	(Heldal and Sjøtun, 2010)
01.12.2006	nm	0.69±0.05	(H.E. Heldal, unpublished data)
Mean		***0.71±0.15***	

2007

During 2007, a total of 17 samples of surface seawater were collected in the Skagerrak, the North Sea and in the Barents Sea and analysed for ^{99}Tc. The results are presented in figure 3.8, and have been reported by NRPA (2009). The ^{99}Tc activity concentrations in the North Sea ranged from 0.17±0.03 to 1.49±0.08 Bq m^{-3}. In the Skagerrak the activity concentrations ranged from 0.45±0.03 to 0.58±0.04 Bq m^{-3}. The highest levels were observed off the east coast of Scotland (1.49±0.08 and 1.38±0.08 Bq m^{-3}). The activity concentrations of ^{99}Tc observed in surface waters of the Norwegian and Barents Seas were in the range 0.19-0.26 Bq m^{-3}.

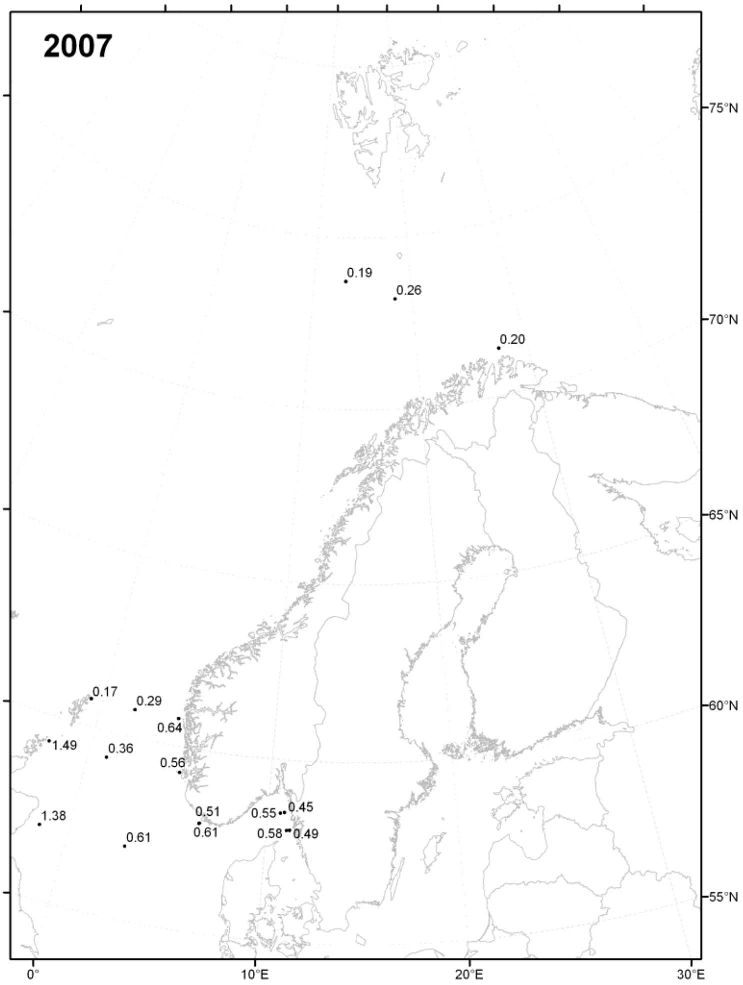


Figure 3.8: Distribution map showing activity concentrations of ^{99}Tc (Bq m^{-3}) in surface seawater samples collected during 2007. The results have previously been reported in NRPA (2009).

2008

During 2008, a total of 30 surface seawater samples were collected in the North, the Norwegian and Barents Sea and analysed for ^{99}Tc. The author of this thesis participated in the analyses of all of the samples collected in the Barents Sea during 2008. The results are presented in figure 3.9, and will be published in (NRPA, 2011). In the northern part of the Norwegian Sea and the Barents Sea the activity concentration of ^{99}Tc ranged from 0.08±0.02 to 0.35±0.04 Bq m^{-3}, and as expected, the highest activity concentrations were observed in the NwCC. In the North Sea the activity concentration of ^{99}Tc ranged from 0.72±0.04 to 1.98±0.09 Bq m^{-3}. The ^{99}Tc level observed at the coastal station Værlandet in 2008 was 0.48±0.04 Bq m^{-3}, which is slightly lower than the level observed in 2006, and a reduction of about 50 % compared to the level observed in May 2003.

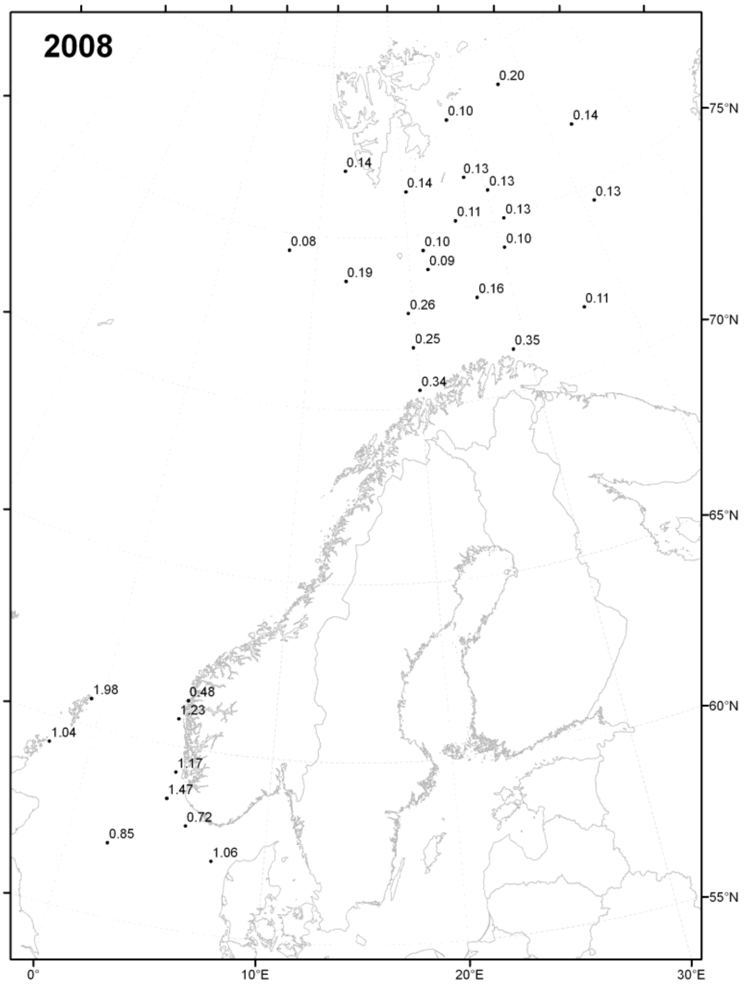


Figure 3.9: Distribution map showing activity concentrations of ^{99}Tc (Bq m^{-3}) in surface seawater samples collected during 2008. The data will be published by NRPA (NRPA, 2011).

2009

During 2009, a total of 22 samples of surface seawater were collected in the Barents Sea, the Norwegian Sea and at the coastal station Værlandet on the west coast of Norway and analysed for ^{99}Tc. The author of this thesis participated in the analyses of 12 of the samples from the Barents Sea. The results are presented in figure 3.10, and will be published in (NRPA, 2011). In the Barents Sea and the Norwegian Sea the activity concentration of ^{99}Tc ranged from 0.06±0.03 (very high uncertainty due to the closeness of the detection limit) to 0.28±0.02 Bq m^{-3}. The highest levels were observed far north in the NwCC. The activity concentrations observed around Svalbard were low (0.07±0.01 – 0.12±0.01 Bq m^{-3}). At Værlandet, the ^{99}Tc activity concentration in seawater was 0.43±0.03 Bq m^{-3}, which is at the same level as observed in 2008.

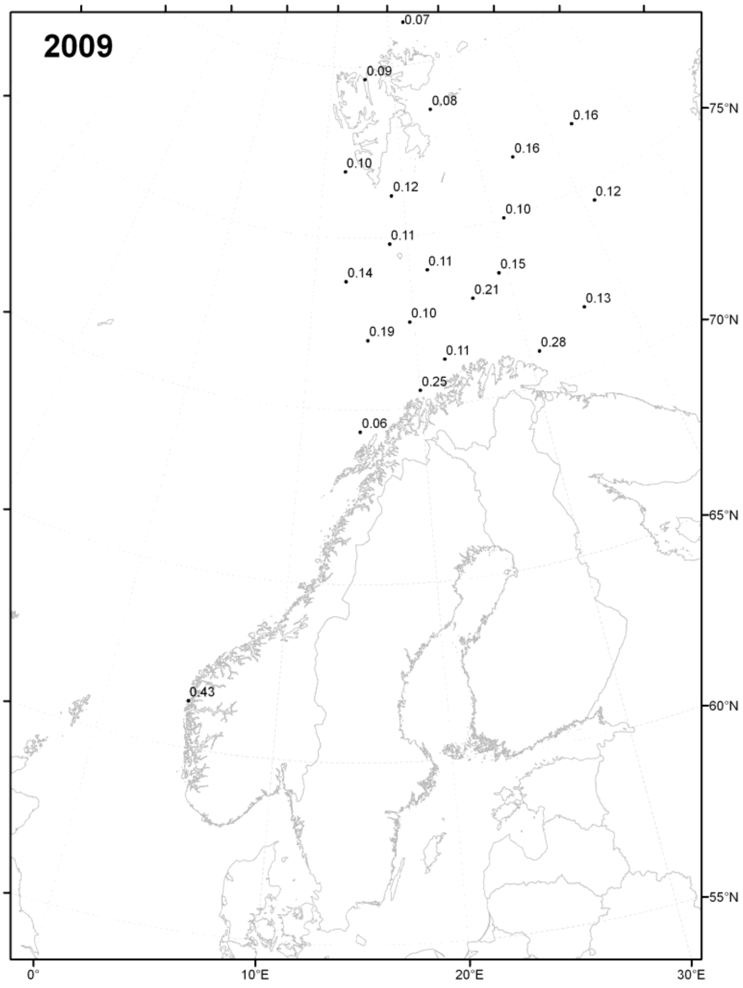


Figure 3.10: Distribution map showing activity concentrations of ^{99}Tc (Bq m^{-3}) in surface seawater samples collected during 2009. The data will be published by NRPA (NRPA, 2011).

2010

In addition to the samples collected in the North Sea during July/August 2010, 6 surface seawater samples collected on three fixed hydrographical transects; the Svinøy- and Gimsøy-transects in the Norwegian Sea, and the Fugløya-Bear Island transect in the Barents Sea, during 2010 have also been analysed for ^{99}Tc (by H. E. Heldal). On each transect one sample was collected in Atlantic water and one sample in coastal water. The ^{99}Tc results from these measurements are presented in figure 3.11 together with the results from the North Sea and Skagerrak. The ^{99}Tc activity concentrations in these samples ranged from 0.12±0.02 to 0.27±0.02 Bq m^{-3}, and the highest activity concentrations were measured in the NwCC.

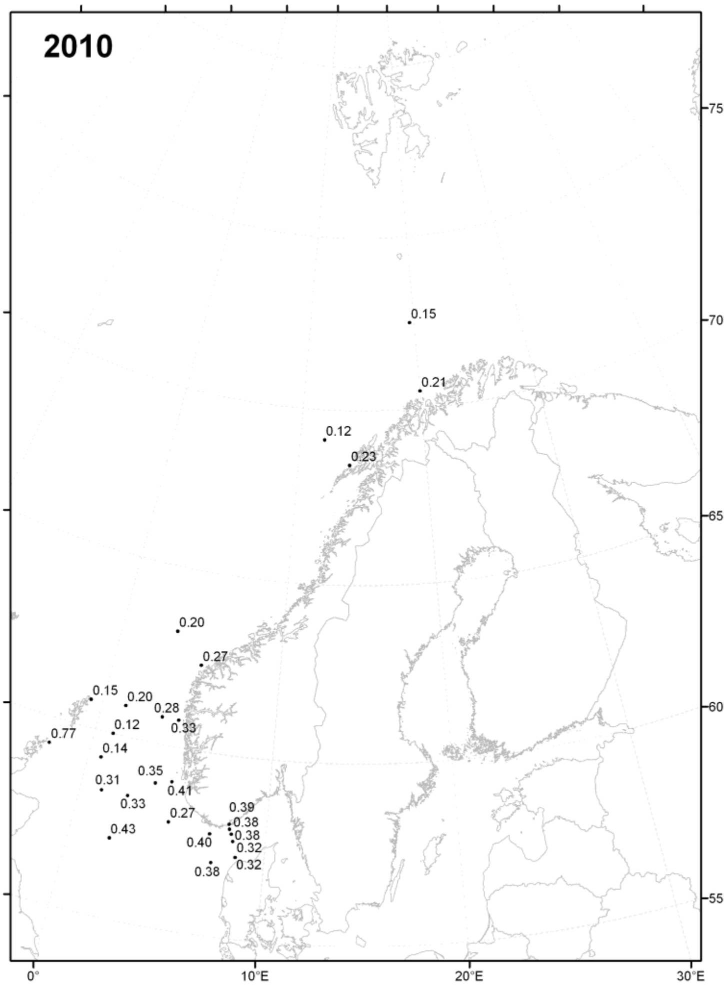


Figure 3.11: Distribution map showing activity concentrations of ^{99}Tc (Bq m^{-3}) in surface seawater samples collected during 2010. The results from the North Sea are also shown in figure 3.1. The six samples collected in the Norwegian and Barents Sea have been analysed in connection with the Norwegian monitoring programme, RAME.

3.3 Time-series of ^{99}Tc in the North and Nordic Seas, 1998 – 2010

Time-series of ^{99}Tc activity concentrations in surface waters in the North and Nordic Seas in the period 1998-2010, based on average activity concentrations for each year, are shown in figure 3.12-18. The data is also given in table 3.3. Note that some of the averages are based on few measurements, and may not represent good averages. The highest levels are measured in samples from the east coast of Britain, the North Sea, Skagerrak and the NwCC, reflecting the closeness to Sellafield and the general circulation pattern of surface water in this area. The activity concentrations in the Norwegian, Greenland and Barents Seas have been generally low (< 1 Bq m^{-3}) during the whole period. Generally, relatively high activity concentrations in the NwCC compared to open sea areas have been observed in all years having comparable observations. The time-series show that the ^{99}Tc activity concentrations in the North and

Nordic Seas are generally decreasing. However, measurements from the North Sea and the NwCC in 2008 showed somewhat higher activity concentrations than anticipated (0.72-1.98 Bq m^{-3}). The reason for this is not clear.

3.3.1 The east coast of Britain and the North Sea

The time-series for of ^{99}Tc at the east coast of Britain and in the North Sea (figure 3.12-3.13) are too short in order to assess a trend, since IMR only have measured samples from 2005, 2007, 2008 and 2010. However, by the Orkney Islands, where ^{99}Tc from Sellafield enters the North Sea, the ^{99}Tc seawater levels have decreased by a factor of two from 2007 (1.49 Bq m^{-3}) to 2010 (0.77 Bq m^{-3}). The 2005 sample from the "east coast of Britain" was not collected by the Orkney Islands like for the other years, but further south- at the west coast of Aberdeen, therefore dilution might explain the somewhat low activity concentration (0.80±0.05 Bq m^{-3}) in 2005.

In the North Sea, the measured ^{99}Tc levels have varied considerably during the five last years. In 2005, the level was quite high with a mean activity concentration of 1.46 Bq m^{-3}. Then the mean activity concentration dropped below 0.4 Bq m^{-3} in 2007, but increased to 1.29 Bq m^{-3} in 2008, a similar level as in 2005. In 2010 the ^{99}Tc level had decreased further to a mean value of about 0.3 Bq m^{-3}.

3.3.2 The Skagerrak

The time-series of ^{99}Tc in the Skagerrak (figure 3.14) consist of measurements from 2003, 2004, 2005, 2006, 2007 and 2010. The ^{99}Tc levels have been relatively constant, around or below 0.5 Bq m^{-3}, except for a peak in 2004 when an activity concentration of 1.03 ± 0.05 Bq m^{-3} was observed outside Arendal. The average ^{99}Tc levels in the Skagerrak in 2006 and 2007 were quite uniform (0.55 and 0.52 Bq m^{-3}, respectively).

3.3.3 The Norwegian Coastal Current south of Stad

For the NwCC south of Stad, the time-series (figure 3.15) consist of measurements from each year in the period 2003-2010.The levels have been relatively uniform, but a moderate decrease (generally speaking) in levels during later years can be seen, except for the unexpected high activity concentrations measured in 2008. In 2008 the variation in the ^{99}Tc observations for this area was considerable high, with a minimum activity concentration of 0.48±0.04 Bq m^{-3} and a maximum of 1.47±0.07 Bq m^{-3} giving a mean value of 1.01±0.40 Bq

m^{-3} (the uncertainty is the standard deviation of the data set). The lowest mean activity concentration in this area was observed in 2010 (0.36±0.06 Bq m^{-3}).

3.3.4 The Norwegian Coastal Current north of Stad

The most interesting time-series, is that of the NwCC north of Stad (figure 3.16), since it is the most extensive (1998-2010). The maximum ^{99}Tc activity concentration was observed in 1999 (1.61±0.07 Bq m^{-3}) but the mean activity concentration was somewhat lower (1.14±0.51 Bq m^{-3}, the uncertainty is the standard deviation of the dataset). The mean ^{99}Tc activity concentration in 2000 (0.81 Bq m^{-3}) was at the same level as in 1998 (0.86 Bq m^{-3}). Unfortunately, like for the rest of the time series, there are no observations from 2001 and 2002. The ^{99}Tc level in 2000 was somewhat lower than in 1999, but increased by a factor of approximately 2.5 from a mean level of 0.53±0.19 Bq m^{-3} in 2003 to mean level of 1.33±0.01 Bq m^{-3} in 2004 (the uncertainties refers to the standard deviations of the data sets). Since the peak level in 2004, the levels have decreased substantially. The mean ^{99}Tc activity concentration in 2009 (0.18±0.11 Bq m^{-3}) was almost one order of magnitude lower than the peak levels observed in 1999 and 2004.

Figure 3.19 presents average activity concentrations of ^{99}Tc in the NwCC north of Stad together with annual discharge of ^{99}Tc from Sellafield. The peak discharge occurred in 1995 (~190 TBq/year). There was also a “minor” discharge peak in 2002 (~85 TBq/year). In seawater from the NwCC, two peaks in the ^{99}Tc activity concentration can be observed, the first in 1999 and the second in 2004.

3.3.5 The Norwegian Sea and the Greenland Sea

The ^{99}Tc activity concentrations in the Norwegian and Greenland Sea in the period 1998 to 2010 are presented in figure 3.17. From the figure it is clear that the mean ^{99}Tc levels have generally been low (below 0.5 Bq m^{-3}) and reasonably constant during the whole period.

3.3.6 The Barents Sea

The time-series for the Barents Sea (2006-2010) in figure 3.18 shows that the activity concentrations of ^{99}Tc have been at a constant, relatively low level (<0.3 Bq m^{-3}) during the whole period.

Table 3.3: ^{99}Tc activity concentrations (Bq m^{-3}) in surface seawater samples from the Nordic Seas in the period 1998-2010. Minimum, maximum and annual mean activity concentrations are given together with number of samples (n). Detailed data are given in Appendix 5.

	^{99}Tc (Bq m^{-3})				
Area / Year	**Min**	**Max**	**Mean**	**n**	**Reference**
The East Coast of Britain					
2005			0.80	1	(H.E Heldal, unpublished data)
2007	1.38	1.49	1.43	2	(NRPA, 2009)
2008			1.04	1	(NRPA, 2011)
2010			0.77	1	(The present study)
The North Sea					
2005	0.90	1.92	1.46	4	(H.E. Heldal, unpublished data)
2007	0.17	0.61	0.36	4	(NRPA, 2009)
2008	0.85	1.98	1.29	3	(NRPA, 2011)
2010	0.12	0.43	0.26	8	(The present study)
Skagerrak					
2003			0.39	1	(Heldal et al., 2007a)
2004			1.03	1	(Heldal et al., 2007a)
2005			0.76	1	(H.E.Heldal, unpublished data)
2006	0.47	0.63	0.55	2	(NRPA, 2008)
2007	0.45	0.58	0.52	4	(NRPA, 2009)
2010	0.32	0.39	0.35	5	(The present study)
NwCC south of Stad					
2003	0.70	1.01	0.85	2	(Heldal et al., 2007a)
2004	0.76	0.77	0.76	2	(Heldal et al., 2007a)
2005	0.81	1.05	0.91	3	(Heldal et al., 2007a) (H.E Heldal, unpublished data)
2006	0.54	1.01	0.70	8	(H.EHeldal,unpublished data)(NRPA, 2009, Heldal and Sjøtun, 2010)
2007	0.51	0.64	0.58	4	(NRPA, 2009)
2008	0.48	1.47	1.01	5	(NRPA, 2011)
2009			0.43	1	(NRPA, 2011)
2010	0.27	0.41	0.34	6	(The present study)
NwCC north of Stad					
1998			0.86	1	(Kershaw et al., 2004)
1999	0.52	1.61	1.14	4	(Kershaw et al., 2004)
2000	0.63	1.19	0.81	11	(Kershaw et al., 2004)
2003	0.36	0.74	0.53	3	(H.E.Heldal, unpublished data)
2004	1.32	1.33	1.33	2	(H.E.Heldal, unpublished data)
2005			0.69	1	(Heldal et al., 2007a)
2006	0.18	0.80	0.47	4	(NRPA, 2008)
2007			0.20	1	(NRPA, 2009)

Table 3.3 (continued): ^{99}Tc activity concentrations (Bq m^{-3}) in surface seawater samples from the Nordic Seas in the period 1998-2010. Minimum, maximum and annual mean activity concentrations are given together with number of samples (n). Detailed data are given in Appendix 5.

Area / Year	**^{99}Tc (Bq m^{-3})**			**n**	**Reference**
	Min	**Max**	**Mean**		
2008	0.34	0.35	0.35	2	(NRPA, 2011)
2009	0.06	0.28	0.18	4	(NRPA, 2011)
2010	0.21	0.27	0.24	3	(H.E.Heldal, unpublished data)
The Norwegian / Greenland Sea					
1998	0.06	0.65	0.23	9	(Kershaw et al., 2004)
1999	0.09	0.26	0.19	8	(Kershaw et al., 2004)
2000	0.05	0.39	0.22	19	(Kershaw et al., 2004)
2003			0.08	1	(H.E. Heldal, unpublished data)
2004	0.05	0.12	0.09	3	(H.E. Heldal, unpublished data)
2006	0.06	0.21	0.11	11	(NRPA, 2008)
2007			0.19	1	(NRPA, 2009)
2008	0.08	0.19	0.13	2	(NRPA, 2011)
2009			0.14	1	(NRPA, 2011)
2010	0.12	0.20	0.16	2	(H.E. Heldal, unpublished data)
The Barents Sea					
2006	0.09	0.15	0.12	2	(NRPA, 2008)
2007			0.26	1	(NRPA, 2009)
2008	0.09	0.26	0.14	17	(NRPA, 2011)
2009	0.07	0.21	0.13	16	(NRPA, 2011)
2010			0.15	1	(H.E. Heldal, unpublished data)

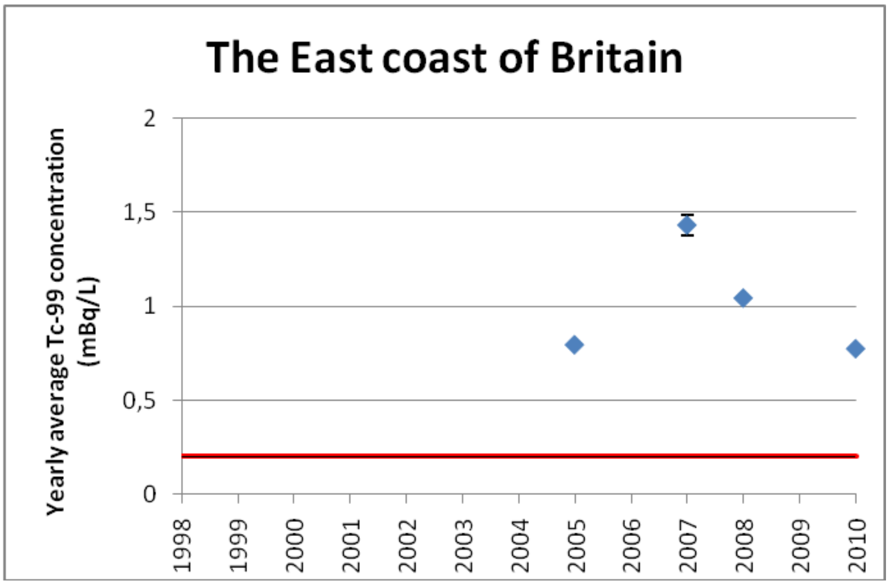


Figure 3.12: Technetium-99 (Bq m^{-3}) in surface waters in the North Sea, off the east coast of Britain. Diamonds show average activity concentrations for each year. Bars show minimum and maximum concentrations. Note that some of the averages are based on few measurements, and may not represent good averages. Red line: pre-EARP ^{99}Tc level of 0.2 Bq m^{-3} in the North Sea at the east coast of Scotland (Leonard et al., 1997). (Note that mBq/L=Bq m^{-3})

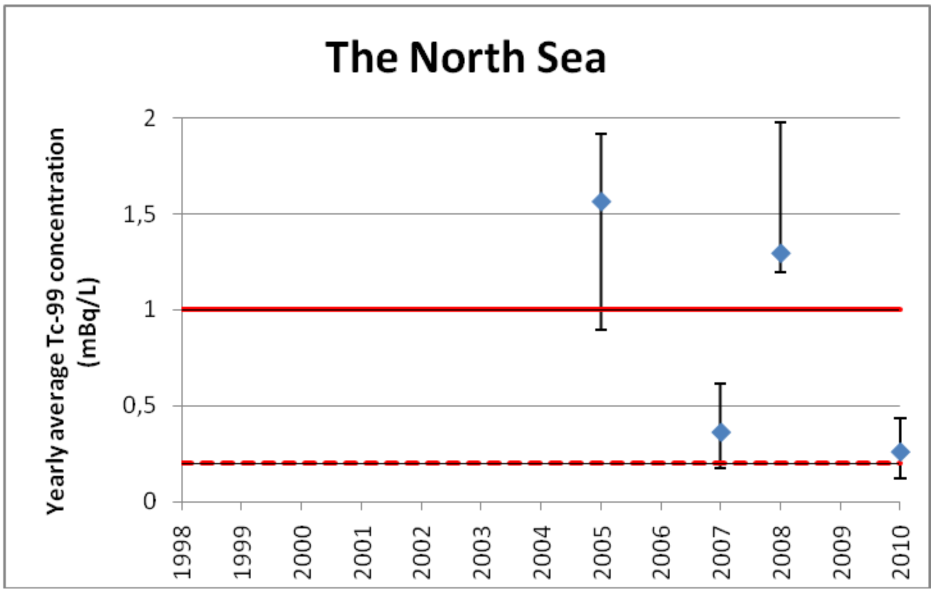
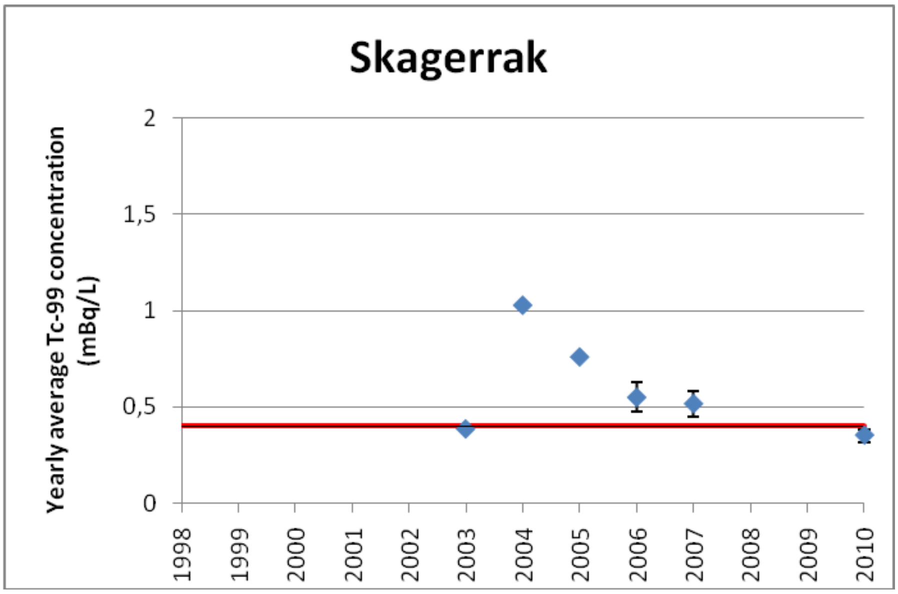


Figure 3.13: Technetium-99 (Bq m^{-3}) in surface waters in the North Sea. Diamonds show average activity concentrations for each year. Bars show minimum and maximum concentrations. Note that some of the averages are based on few measurements, and may not represent good averages. Solid red line: pre-EARP level of 1 Bq m^{-3} (Herrmann et al., 1995). Dashed red line: pre-EARP ^{99}Tc level of 0.2 Bq m^{-3} in the North Sea (Leonard et al., 1997). (Note that mBq/L=Bq m^{-3})



Figur 3.14: Technetium-99 (Bq m^{-3}) in surface waters in the Skagerrak. Diamonds show average activity concentrations for each year. Bars show minimum and maximum concentrations. Note that some of the averages are based on few measurements, and may not represent good averages. The red line represents the pre-EARP ^{99}Tc level of 0.4 Bq m^{-3} (Herrmann et al., 1995). (Note that mBq/L=Bq m^{-3})

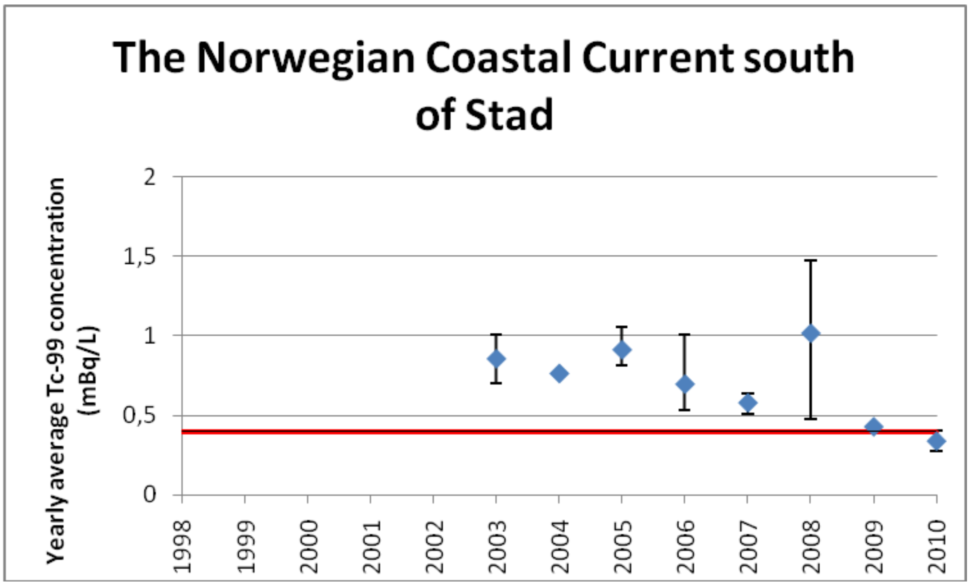


Figure 3.15: Technetium-99 (Bq m^{-3}) in surface waters in the NwCC south of Stad. Diamonds show average activity concentrations for each year. Bars show minimum and maximum concentrations. Note that some of the averages are based on few measurements, and may not represent good averages. The red line represents the pre-EARP ^{99}Tc level of 0.4 Bq m^{-3} (Herrmann et al., 1995). (Note that mBq/L=Bq m^{-3})

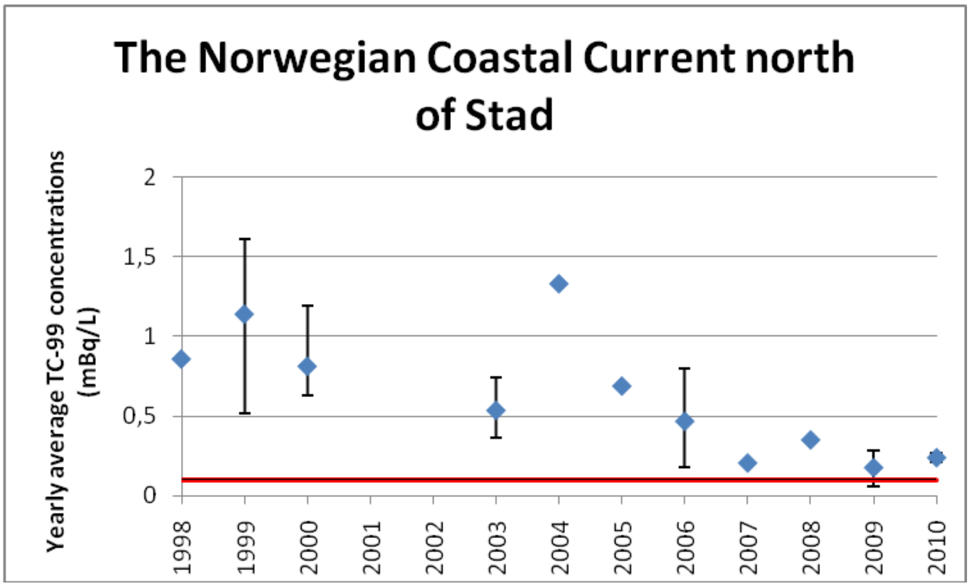


Figure 3.16: Technetium-99 (Bq m^{-3}) in surface waters in the NwCC north of Stad. Diamonds show average activity concentrations for each year. Bars show minimum and maximum concentrations. Note that some of the averages are based on few measurements, and may not represent good averages. Red line: pre-EARP ^{99}Tc level of 0.1 Bq m^{-3} (Kershaw et al., 1999). (Note that mBq/L=Bq m^{-3})

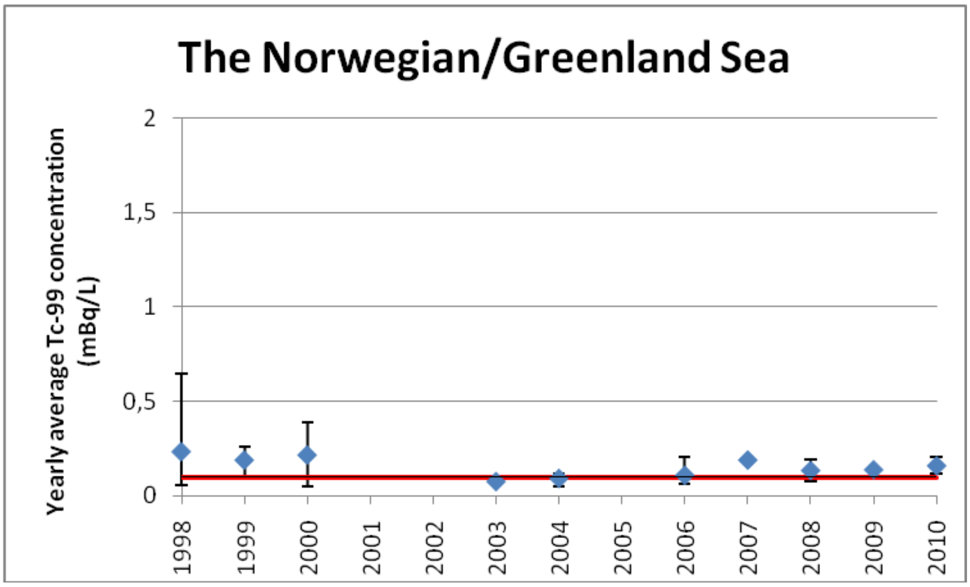


Figure 3.17: Technetium-99 (Bq m^{-3}) in surface waters in the Norwegian/Greenland Sea. Diamonds show average activity concentrations for each year. Bars show minimum and maximum concentrations. Note that some of the averages are based on few measurements, and may not represent good averages. A few samples from the Norwegian/Greenland Sea had activity concentrations below the detection limit. These are not included in the calculation of average concentrations. Red line: pre-EARP ^{99}Tc level of 0.1 Bq m^{-3} (Kershaw et al., 1999). (Note that mBq/L=Bq m^{-3})

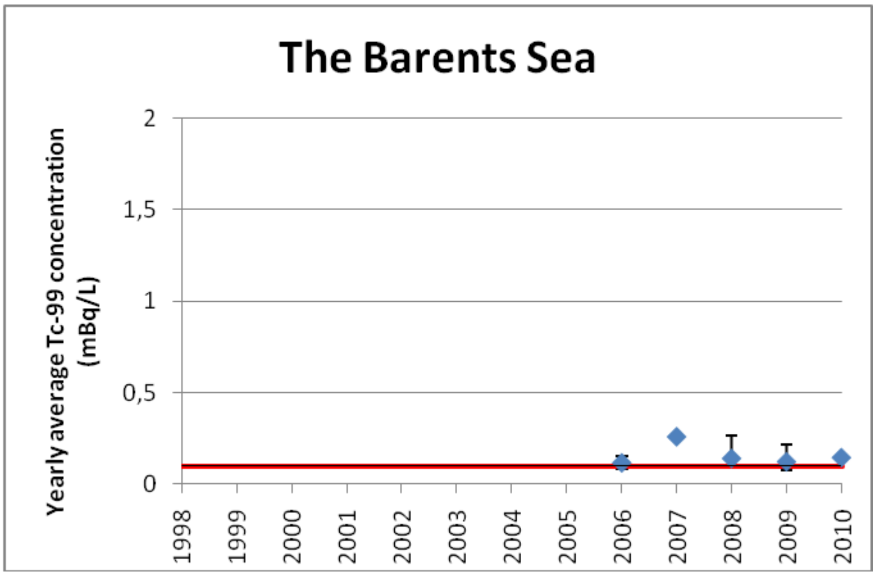


Figure 3.18: Technetium-99 (Bq m^{-3}) in surface waters in the Barents Sea. Diamonds show average activity concentrations for each year. Bars show minimum and maximum concentrations. Note that some of the averages are based on few measurements, and may not represent good averages. Red line: pre-EARP ^{99}Tc level of 0.1 Bq m^{-3} (Kershaw et al., 1999). (Note that mBq/L=Bq m^{-3})

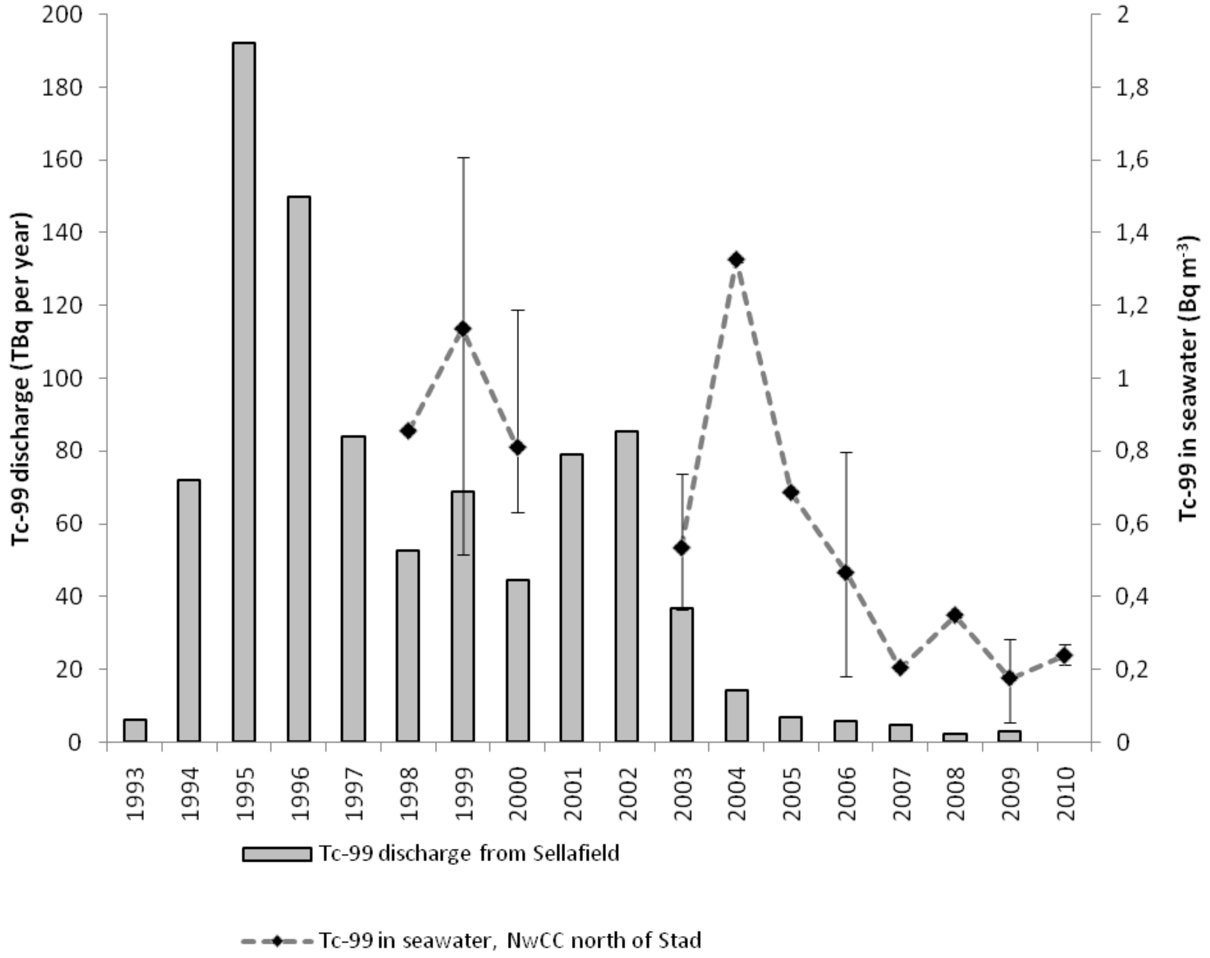


Figure 3.19: Activity concentrations of ^{99}Tc (Bq m^{-3}) in the Norwegian coastal current north of Stad in the periods 1998-2000 and 2003-2009, and annual discharge of ^{99}Tc from Sellafield (TBq per year).

3.3.7 ^{99}Tc in seawater from Værlandet

The results from the measurements of ^{99}Tc from seawater from the fixed coastal station at Værlandet (figure 3.20) are given in table 3.4. The results are graphically presented in figure 3.21. From the figure, a general decrease in observed ^{99}Tc activity concentrations in the period 2003 to 2010 can be seen.

Figure 3.20: Map showing the location of Værlandet. The map has been created using the map application of the Directorate of Fisheries, Fiskeridirektoratet (http://kart.fiskeridir.no/).

Table 3.4: Sampling dates, position and activity concentrations of ^{99}Tc (Bq m^{-3}) in surface seawater samples from Værlandet. Relative errors in the measurements are in the range of 4-8 %.

Programme	Area	Sampling depth (m)	Date	Latitude	Longitude	^{99}Tc (Bq m^{-3})	± (Bq m^{-3})
Radnor	Værlandet	1	19.05.2003	61,30	4,80	1.01	0.04
Radnor	Værlandet	1	01.12.2003	61,30	4,80	0.70	0.03
Radnor	Værlandet	1	10.05.2004	61,30	4,80	0.76	0.03
Radnor	Værlandet	1	23.11.2006	61,30	4,80	0.62	0.03
RAME	Værlandet	1	27.10.2008	61,30	4,80	0.48	0.04
RAME	Værlandet	1	16.11.2009	61,30	4,80	0.43	0.03

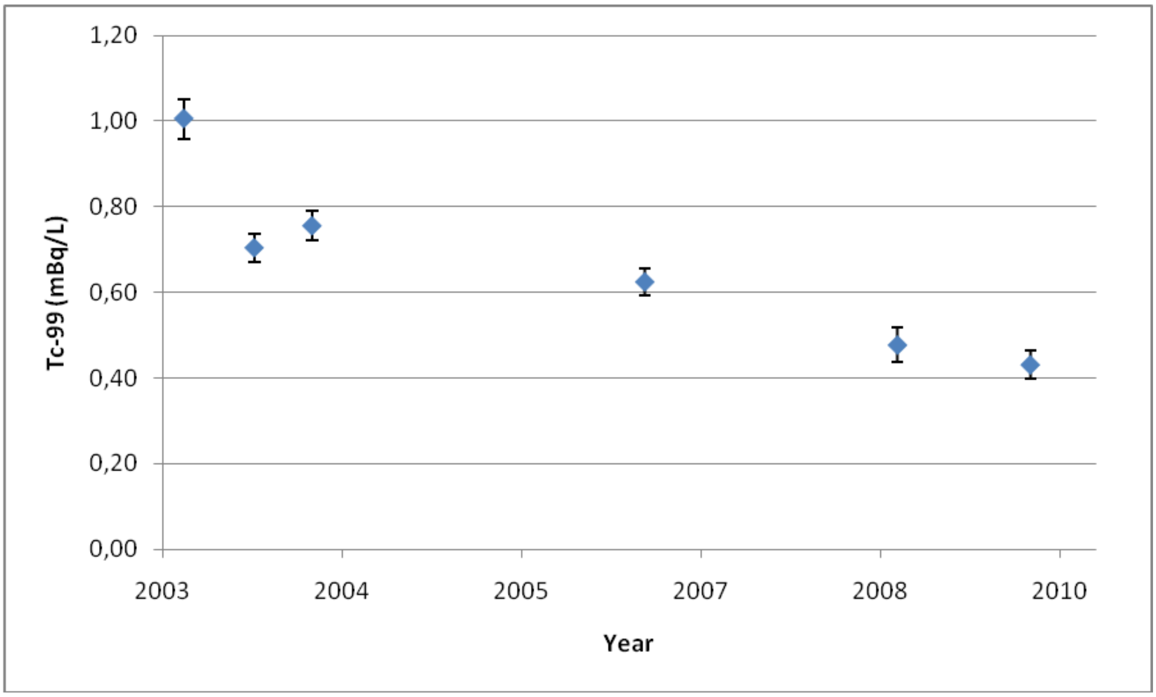


Figure 3.21: Time-serie of ^{99}Tc activity concentrations (Bq m^{-3}) at Værlandet station in the period 2003-2010 (there are no data for 2005 and 2007). Error bars show absolute uncertainty in the measurements (± Bq m^{-3}).

4. Discussion

In chapter 4.1, the spatial and temporal distribution of ^{99}Tc in the North and Nordic Seas are discussed. The ^{99}Tc activity concentrations in different sea areas are discussed in relation to available hydrographic data (salinity and temperature), and transit times and transfer factors from Sellafield to Norwegian waters are briefly discussed. Information on ^{99}Tc/^{137}Cs-ratios in different sea areas is also included. Next, in chapter 4.2, the fate of ^{99}Tc in the marine environment is discussed. Firstly, information on uptake in marine organisms is given. It is important to have knowledge about the uptake of ^{99}Tc in biota in order to evaluate the environmental consequences of elevated ^{99}Tc seawater activity concentrations. Secondly, the binding of ^{99}Tc in sediments are discussed, as the geochemical behaviour of this radionuclide depends on redox conditions. In chapter 4.3, the objectives of the OSPAR commission concerning radioactive substances are discussed in relation to the reduction in ^{99}Tc discharges from Sellafield and the following decrease in seawater activity concentrations in the North and Nordic Seas. Finally, an evaluation of the analytical method used in the present study is given in chapter 4.4.

4.1 ^{99}Tc activity concentrations in seawater

4.1.1 Spatial and temporal distribution of ^{99}Tc in the North Sea, Skagerrak and the NwCC south of Stad

The IMR data on ^{99}Tc activity concentrations in seawater in the North Sea, Skagerrak and the NwCC south of Stad are mainly in good agreement with other observations (e.g. NRPA, 2005, NRPA, 2006, Nies et al., 2009). Table 4.1 presents minimum, maximum and average annual activity concentrations of ^{99}Tc in the above mentioned areas in the period 1996 to 2010 from the literature and the present study.

From table 4.1, it can be seen that ^{99}Tc levels in the North Sea (including the east coast of Britain and the NwCC south of Stad) have decreased by approximately a factor of ten, from a mean level of approximately 3.3 Bq m^{-3} in 1999 (Nies et al., 2000, Rudjord et al., 2001) to 0.33 Bq m^{-3} in 2010.

The ^{99}Tc activity concentration observed in the present study at the west coast of the Orkney Islands in July 2010 (0.77 Bq m^{-3}, table 3.1) is the lowest measured in this area since elevated post-EARP concentrations were first observed in 1994 (1.6 Bq m^{-3}) (Leonard et al., 1997). By contrast, Brown et al. (1999) reported values up to 7 Bq m^{-3} at the east coast of Scotland in November 1996. However, the ^{99}Tc level in this area is still considerably higher today than before 1994 (0.1 – 0.2 Bq m^{-3} off the Scottish coast in 1992 and 1993 (Leonard et al., 1997)).

The average ^{99}Tc concentrations in the NwCC south of Stad and the Skagerrak in 2010 were 0.34 and 0.35 Bq m^{-3}, respectively. These results are similar to the levels reported by Herrmann et al. (1995) of 0.4 and 0.3 Bq m^{-3} in the NwCC and the Skagerrak, respectively, in July 1991 (before EARP began operation). The main source of ^{99}Tc at that time was discharges from the French reprocessing plant La Hague, since the ^{99}Tc discharges from La Hague were greater than those from Sellafield during the 1980s. Although the ^{99}Tc levels are decreasing, they are considerably higher than the ‘fallout background level’ of 0.005 Bq m^{-3} reported for oceanic Atlantic water reported by Dahlgaard et al. (1995).

Table 4.1: ^{99}Tc activity concentrations in surface seawater (Bq m^{-3}) in the North Sea, Skagerrak and NwCC south of Stad in the period 1996 to 2010; literature data and selected IMR-data included in the discussion. n = number of samples. NwCC s = Norwegian Coastal Current south of Stad.

Year	Area	^{99}Tc (Bq m^{-3})			n	Reference
		Min	Max	Mean		
1996	The North Sea and NwCC s	0.3	8.5	2.67	22	(Brown et al., 1999)
1997	The North Sea and NwCC s	0.2	6.5	2.42	19	(Brungot et al., 1999)
1997	Skagerrak	0.4	1.7	1.18	5	(Brungot et al., 1999)
1997	The North Sea	0.1	7.1	3.25	30	(Nies et al., 2000)
1999	The North Sea	0.46	7.2	3.62	7	(Rudjord et al., 2001)
1999	The North Sea	0.1	6.8	2.20	25	(Nies et al., 2000)
2000	Skagerrak	0.89	1.33	1.15	4	(Kolstad and Lind, 2002)
2001	The North Sea and NwCC s	0.22	7.3	2.05	35	(Kolstad and Lind, 2002)
2001	Skagerrak	0.65	1.60	0.89	6	(Kolstad and Lind, 2002)
2002	Skagerrak	1.3	2.05	1.69	3	(NRPA, 2004)
2003	Skagerrak	1.1	1.7	1.4	4	(NRPA, 2005)
2003	Skagerrak (Arendal)			0.39	1	(Heldal et al., 2007a)
2004	The North Sea	0.11	3.3	1.41	15	(NRPA, 2006)
2004	NwCC s	1.4	1.6	1.5	3	(NRPA, 2006)
2004	NwCC s (Værlandet and Tysnes)	0.76	0.77	0.77	2	(Heldal et al., 2007a)
2004	Skagerrak	0.60	1.3	0,94	4	(NRPA, 2006)
2004	Skagerrak (Arendal)			1,03	1	(Heldal et al., 2007a)

Table 4.1 (continued): ^{99}Tc activity concentrations in surface seawater (Bq m^{-3}) in the North Sea, Skagerrak and NwCC south of Stad in the period 1996 to 2010; literature data and selected IMR-data included in the discussion. n = number of samples. NwCC s = Norwegian Coastal Current south of Stad.

Year	**Area**	**^{99}Tc (Bq m^{-3})**			**n**	**Reference**
		Min	**Max**	**Mean**		
2005	The North Sea and NwCC s	0.80	1.92	1.22	8	(Heldal, unpublished data)(Heldal et al., 2007a)
2005	Skagerrak/Kattegat			0.76	1	(Heldal, unpublished data)
2005	The North Sea and NwCC s	0.13	2.08	1.18	40	(Nies et al., 2009)
2006	Skagerrak	0.45	0.63	0.54	6	(NRPA, 2008)
2007	The North Sea and NwCC s	0.17	1.49	0.66	10	(NRPA, 2009)
2007	Skagerrak	0.45	0.58	0.52	4	(NRPA, 2009)
2008	The North Sea and NwCC s	0.72	1.98	1.11	9	(NRPA, 2011)
2010	The North Sea, NwCC s, and Skagerrak	0.12	0.77	0.33	20	The present study

The ^{99}Tc activity concentrations in the North Sea and the NwCC south of Stad found in 2008 (0.72 to 1.98 Bq m^{-3}) (NRPA, 2011) were generally higher than the levels observed in 2007 (0.17 to 1.49 Bq m^{-3}) (NRPA, 2009), and the reasons for these unexpected observations are not fully clear. The highest activity concentration (1.98 Bq m^{-3}) was observed in a sample from the north-east coast of the Shetland Islands. This is an anomalous observation based on the fact that this location is not on the route that radionuclides from Sellafield normally follow (see figure 2.2). Table 4.2 shows ^{99}Tc activity concentrations and hydrographic data for samples collected at the north-eastern coast of the Shetland Islands in 2007, 2008 and 2010. It can be seen that the salinity in 2008 was lower (<35) than in the samples collected in 2007 and 2010. The 2007 and 2010 results represent the “expected” situation at this sampling location with inflowing high salinity, ^{99}Tc-poor Atlantic water. The low salinity (<35) in the 2008-sample, however, indicates that it was not associated with Atlantic water, suggesting that coastal water from the Irish Sea labelled with Sellafield radionuclides had taken a different route to the North Sea at the time of sampling.

Table 4.2: ^{99}Tc concentrations, salinities, temperatures and depths of samples collected at a station on the north-east coast of the Shetland Islands in 2007, 2008 and 2010.

Ship	**Station**	**Sampling date**	**Position**		**Depth (m)**	**Sampling depth (m)**	**Salinity**	**Temp (°C)**	**^{99}Tc (Bq m^{-3})**
			Lat	**Long**					
J.Hjort	379	13.04.07	60.75 N	-0.66 W	95	5	35.3320	8.6	0.17±0.03
J.Hjort	622	29.07.08	60.75 N	-0.66 W	100	5	34.5965	13.4	1.98±0.09
J.Hjort	624	31.07.10	60.76 N	-0.68 W	109	5	35.2444	12.4	0.15±0.01

Results from each cruise represent only a “snap shot” picture of the distribution of ^{99}Tc at the particular sampling time. The weather conditions changes over time, as does the influence of different water masses to a specific area. It is thought that wind forcing plays a main role in the advection of radionuclides (McCubbin et al., 2002). Fluctuations in ^{99}Tc levels in the short term could also in part be due to the pulsed nature in the discharges from Sellafield (McCubbin et al., 2002).

When comparing activity concentrations in samples collected at coastal stations (Arendal, Tysnes, Espegrend, Værlandet, Rørvik) with activity concentrations in samples collected from ships, care must be taken. At the coastal stations, samples are most often collected from shore and taken in the upper surface (0 m), while the samples collected from ships are sub-surface samples (5-6 m). Coastal samples collected near shore will most likely have lower salinity and lower activity concentrations due to dilution of the seawater from precipitation and other fresh water run-off from land compared to samples collected from ships. Also, if samples are collected in sheltered areas, the radionuclide concentrations may be lower due to little inflow of saline, ^{99}Tc-rich seawater. Low salinity water has lower density than high salinity water, and will therefore lie on top of the denser, saltier water.

The difference between the coastal and open sea samples can be seen for the 2003 samples. The ^{99}Tc activity concentration in the only IMR-sample collected in the Skagerrak area (Arendal) in 2003 (0.39 Bq m^{-3}) was 3-4 times lower than the reported ^{99}Tc results from NRPA (range 1.1 to 1.7 Bq m^{-3}) in samples collected off the south-eastern coast of Norway (NRPA, 2005). The IMR-sample was collected by a fisherman, and the exact sampling location is not known. The sample was, however, most probably collected from the upper surface (0 m). It is therefore assumed that the NRPA results are giving a more representative picture of the ^{99}Tc levels in the Skagerrak area in 2003.

In 2004, a ^{99}Tc activity concentration of 1.03 Bq m^{-3} was measured in a sample from Arendal (figure 3.5), which is in better agreement with the Skagerrak 2004-level (0.60-1.3 Bq m^{-3}) reported by NRPA (2006). The IMR ^{99}Tc activity concentration in the NwCC south of Stad in 2004 was 0.76 Bq m^{-3} (Værlandet) and 0.77 Bq m^{-3} (Tysnes). In comparison, NRPA (2006) reported somewhat higher levels of ^{99}Tc in this area for 2004 (range from 1.4 to 1.6 Bq m^{-3}). The lower concentrations in the IMR-samples may be due to the fact that the samples were collected at coastal stations, while the NRPA samples were collected in open sea areas.

The IMR ^{99}Tc results for the five samples collected in the North Sea during November 2005 are in very good agreement with the results reported by Nies et al. (2009), from a cruise during August 2005, see figure 4.1 and table 4.1. Both found relatively high ^{99}Tc activity concentrations in the central North Sea (around 1.90 Bq m^{-3}), and lower concentrations further north. The high concentrations in the southern central North Sea reflect earlier higher discharge of ^{99}Tc from Sellafield, which have later been reduced. The different activity concentrations in the central and northern part of the North Sea may be due to differences in seawater residence time. The mean residence time of seawater in the North Sea is about 1 to 2 years, but the residence time is generally higher in the southern part compared to the northern part (SafetyAtSea, 2011). This is because there is more rapid exchange in the northern part due to inflow of Atlantic water.

The results from Nies et al. (2009) also confirmed that the low discharges from the La Hague reprocessing plant has a minor impact on ^{99}Tc level in the North Sea compared to Sellafield during the mid 2000’s; ^{99}Tc activity concentrations in the English Channel ranged from 0.03 to 0.55 Bq m^{-3} and were mainly below 0.1 Bq m^{-3}.

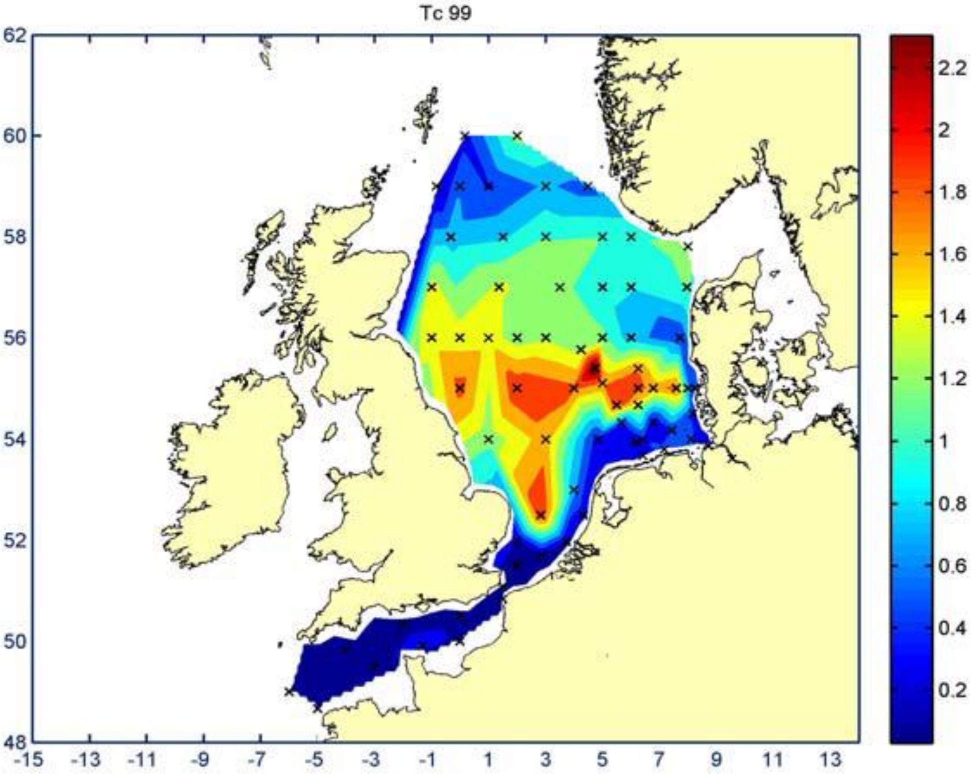


Figure 4.1: Spatial distribution of ^{99}Tc (Bq m^{-3}) in the North Sea during August 2005 (Nies et al., 2009).

The 2005 IMR ^{99}Tc activity concentrations in samples from the eastern part of the North Sea, close to the entrance of Skagerrak, and the border between Skagerrak and Kattegat (1.90 and 0.76 Bq m^{-3}, respectively) (figure 3.6) corresponds well with the ^{99}Tc activity concentrations in the Skagerrak in 2005 reported by NRPA (2007) (range 0.7 to 1.5 Bq m^{-3}). The lower activity concentration in the sample from Kattegat (0.76 Bq m^{-3}) can be explained by dilution of the ^{99}Tc signal. The inflowing North Sea water (high ^{99}Tc signal) with a high salinity (34.5) (Appendix 5) mixes with brackish outflowing Baltic Sea water (low ^{99}Tc signal) in the Kattegat, giving a lower salinity (27.8) (Appendix 5) and a dilution of the tracer signal.

In addition to horizontal transport of ^{99}Tc along with surface currents (advection), a fraction of ^{99}Tc is also transported vertically down in the water column. Figure 4.2 shows the vertical distribution of ^{99}Tc at sampling location 514 (57.86 N, 5.80 E) in the North Sea / NwCC in 2008 together with hydrographical data (salinity and temperature). Salinity and temperature can be used to identify water masses. From the salinity and temperature "profiles" it can be seen that the surface layer (5 m) has a lower salinity and higher temperature compared to the denser bottom water (200 m). The activity concentration in the surface sample (0.72 Bq m^{-3}, see figure 3.9) is 2.5 times the activity concentration in the bottom sample (0.29 Bq m^{-3}, see Appendix 5). Thus, ^{99}Tc activity concentration and salinity is inversely related, while activity concentration is positive correlated with temperature. The low-salinity coastal water bearing the radiotracer signal is mixed with inflowing high salinity Atlantic water. The less dense coastal water, with higher temperature and lower salinity than the inflowing water, remains close to the surface. The lower ^{99}Tc activity concentration in the bottom samples suggested that ^{99}Tc is not distributed / mixed uniformly in the water column. In a study from the western Irish Sea, Leonard et al. (2004) also found that ^{99}Tc activity concentrations were inversely related to the water salinity due to incomplete mixing of ^{99}Tc within the water column.

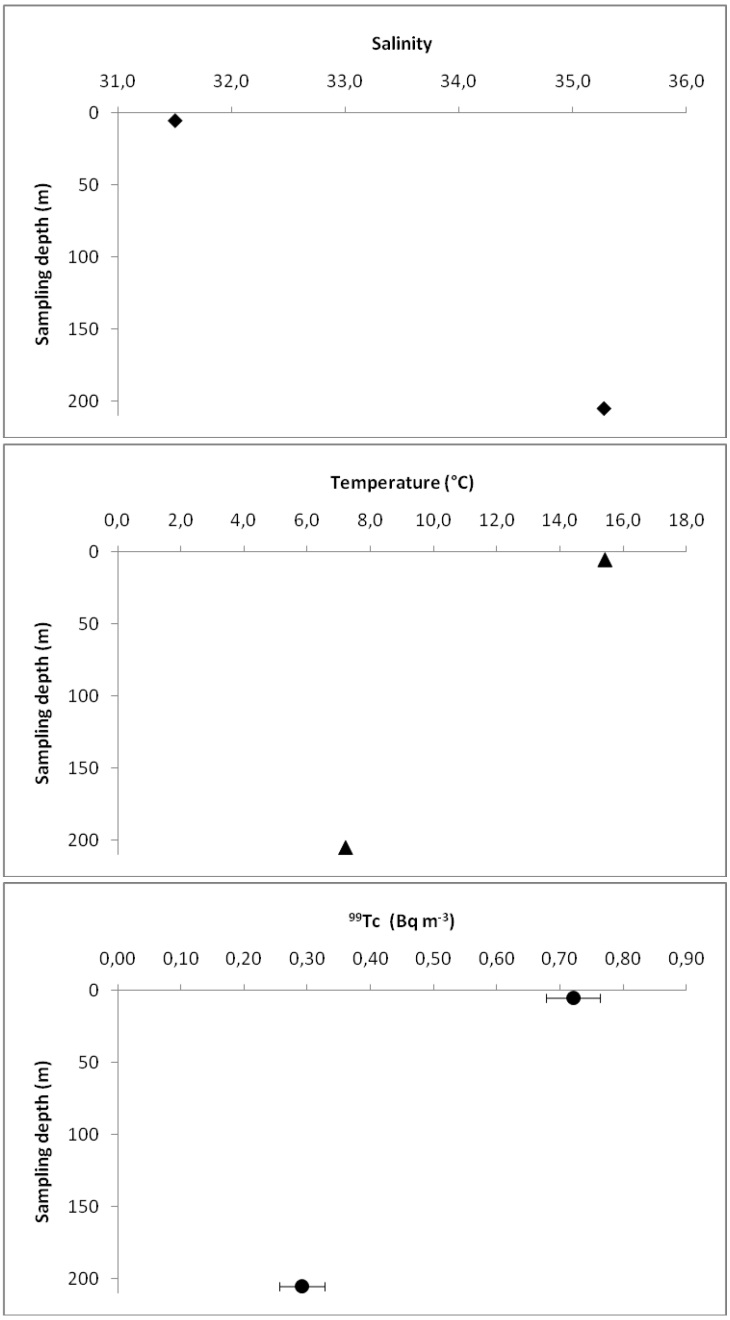


Figure 4.2: ^{99}Tc (Bq m^{-3}) in surface and bottom samples at sampling location 514 (57.86 N, 5.80 E) in the North Sea / NwCC in 2008 together with hydrographical data (salinity and temperature). (NRPA, 2011, Appendix 5)

4.1.2 Spatial and temporal distribution of ^{99}Tc in the Norwegian, Greenland and Barents Seas and the NwCC north of Stad

Due to dilution of the tracer signal, the ^{99}Tc activity concentrations in surface seawater are decreasing when following the NwCC northwards along the Norwegian coast. Consequently, the ^{99}Tc levels in the Norwegian, Greenland and Barents Seas are lower than in the North Sea. The surface seawater ^{99}Tc activity concentration of about 0.2 Bq m^{-3} in the NwCC north of Stad in 2010 (the present study), corresponds to a dilution factor (seawater activity concentration at the point-source/activity concentration at a sampling location downstream *t* years later) of approximately 185 for the Sellafield discharges to the northern Norwegian coastal waters, assuming a ^{99}Tc seawater activity concentration of ~ 37 Bq m^{-3} (Nies et al., 2009) close to the Sellafield site in 2006 (using a transit time *t* of about 4 years).

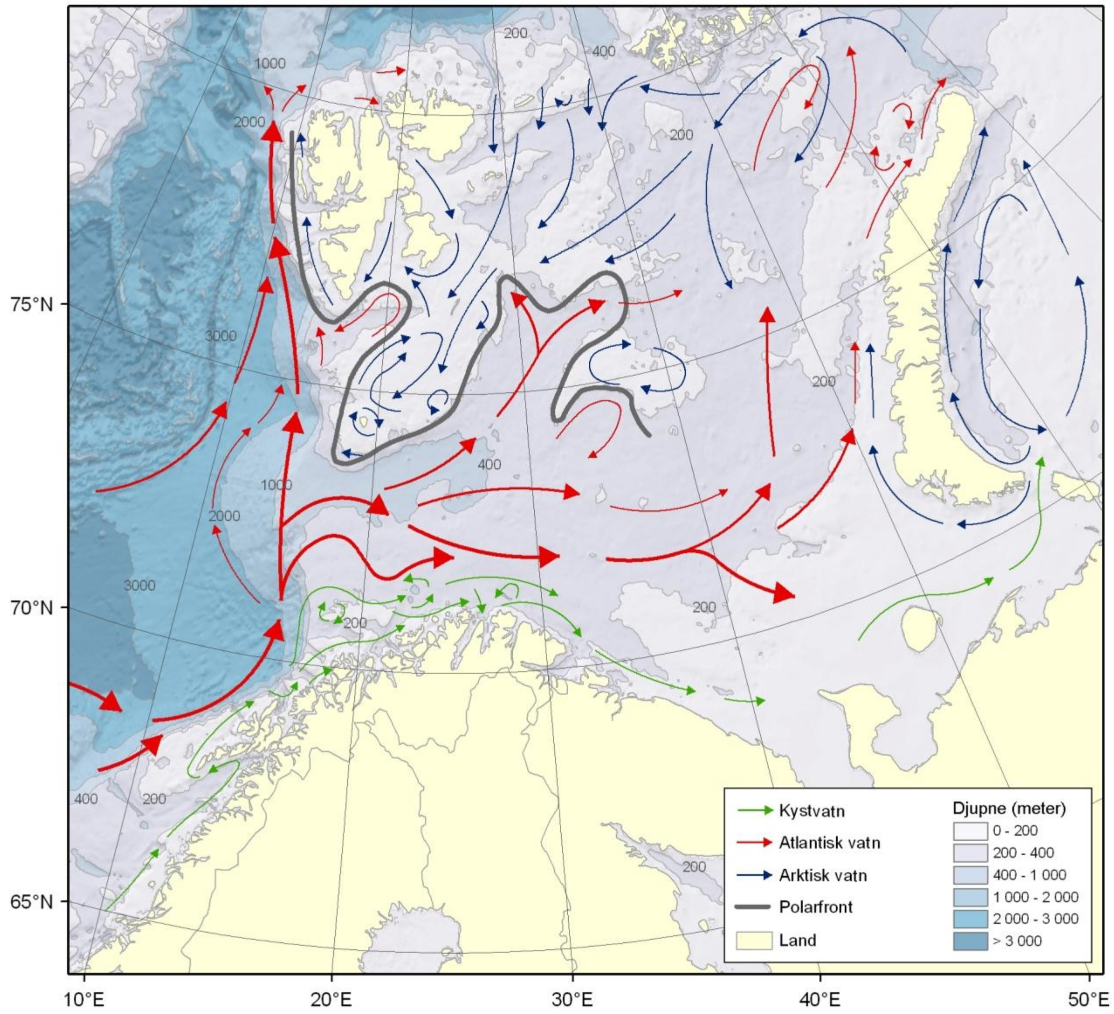
The ^{99}Tc results from the Norwegian / Greenland Sea (figure 3.3) published by Kershaw et al. (2004), confirmed that the EARP plume had reached Arctic waters by 2000. In 2001, NRPA measured ^{99}Tc levels in the Norwegian Arctic marine environment to be in the range 0.13 to 0.36 Bq m^{-3} (Dowdall et al., 2003), at the same level as reported by Kershaw et al. (2004) for the Norwegian/Greenland Sea one year earlier. The present study indicates that the ^{99}Tc levels in the Norwegian/Greenland and Barents Sea have decreased to a relatively constant average level of about 0.10-0.15 Bq m^{-3} in the period 2003 - 2010 (figure 3.17 and 3.18). Although the activity concentrations in these areas are considered low (around the pre-EARP level of ~0.1 Bq m^{-3} (Kershaw et al., 1999)), the present levels are still 20-30 times higher than the ‘fallout background level’ of 0.005 Bq m^{-3} (Dahlgaard et al., 1995).

Figure 4.3 shows the main features of the circulation of the Barents Sea. The grey line represents the Polar Front that arises to east of the West Spitsbergen Current (WSC) where the warm, high salinity Atlantic water from south and west meets the cold, less saline Arctic water from north and east. In this area the seawater temperature and salinity varies much over short distances (Gjøsæter et al., 2009). The polar front is extending to the area south of Bear Island (figure 4.3).

The Fugløya-Bear Island transect defines the border between the Norwegian Sea and the Barents Sea (Morten D. Skogen, pers. comm.). Kershaw et al. (2004) reported an approximate transit time of 4.5 years for EARP related ^{99}Tc to this region, in agreement with the transit time of ~5 years from Sellafield to the WSC as reported by Dahlgaard (1995) (based on ^{137}Cs distribution). The ^{99}Tc level at Fugløya in 1994 was 0.14 Bq m^{-3} (Kershaw et al., 1999). In 1998, the ^{99}Tc activity concentration at this location was 0.86 Bq m^{-3} (figure 3.3 a), 6 times higher than the 1994 pre-EARP level (Kershaw et al., 2004). The ^{99}Tc activity concentrations at Fugløya in 2008, 2009 and 2010 (0.34, 0.25 and 0.21 Bq m^{-3}, respectively) (Figure 3.9, 3.10 and 3.11) were approximately two times higher than the pre-EARP concentration. Thus, even though the ^{99}Tc level has declined during the last decade, it is still higher than the 1994 “background” level. Further offshore on the Fugløya – Bear Island transect, the ^{99}Tc activity concentrations were lower; 0.25-0.26, 0.10 and 0.15 Bq m^{-3} in 2008, 2009 and 2010, respectively (figure 3.9, 3.10 and 3.11), consistent with inflowing Atlantic water (salinity >35) diluting the radiotracer signal. The lower levels in 2009 and 2010 than in 2008 are due to the reduced ^{99}Tc discharges from Sellafield in 2004.

In 2008 the ^{99}Tc activity concentrations in the NwCC in the Barents Sea were 0.34 and 0.35 Bq m^{-3}, while activity concentrations in open sea areas were lower; around 0.10 to 0.20 Bq m^{-3} (see figure 3.9). These ^{99}Tc levels were similar to or lower than the levels observed in the same area in 2005 by NRPA (0.1 - 0.7 Bq m^{-3}) (NRPA, 2007). The average ^{99}Tc activity concentration in the Barents Sea in 2009 was 0.13 Bq m^{-3} (table 3.3).

The activity concentrations in the NwCC are higher compared to the levels in open sea areas in the northern part of the Barents Sea and east off Svalbard, reflecting the current patterns in the Barents Sea (figure 4.3). ^{99}Tc activity concentrations of ~ 0.10 Bq m^{-3} (similar to the 1994 “background” level reported by Kershaw et al. (1999)) were measured in surface samples collected off the east coast of Svalbard in 2008 and 2009. These seawater samples had temperatures below 1°C and salinities around 32-33 (well below 34.5), clearly identifying the water mass as polar water (Kershaw et al., 2004). The coastal water with three times higher ^{99}Tc activity concentrations had higher temperatures (around 9°C) and salinities (around 34).



Figur 4.3: Circulation of surface waters in the Barents Sea. Red arrows: Atlantic water. Blue arrows: Arctic water. Green arrows: Coastal water. Data source: (Gjøsæter et al., 2009)

Vertical distribution of ^{99}Tc in the Barents Sea

Figure 4.4 shows the vertical distribution of ^{99}Tc at sampling location 404 (71.25 N, 28.73 E) in the Barents Sea / NwCC in 2008 together with hydrographical data. The surface water is typical NwCC water with salinity 34.4 and temperature 9.2 °C, carrying along radionuclides originating from Sellafield. The denser bottom water is colder (4.6°C) and influenced by high salinity (35.06), radionuclide poor Atlantic water. The ^{99}Tc activity concentration in the bottom sample (0.16 Bq m^{-3}) was approximately 2 times lower than in the surface sample (0.35 Bq m^{-3}).

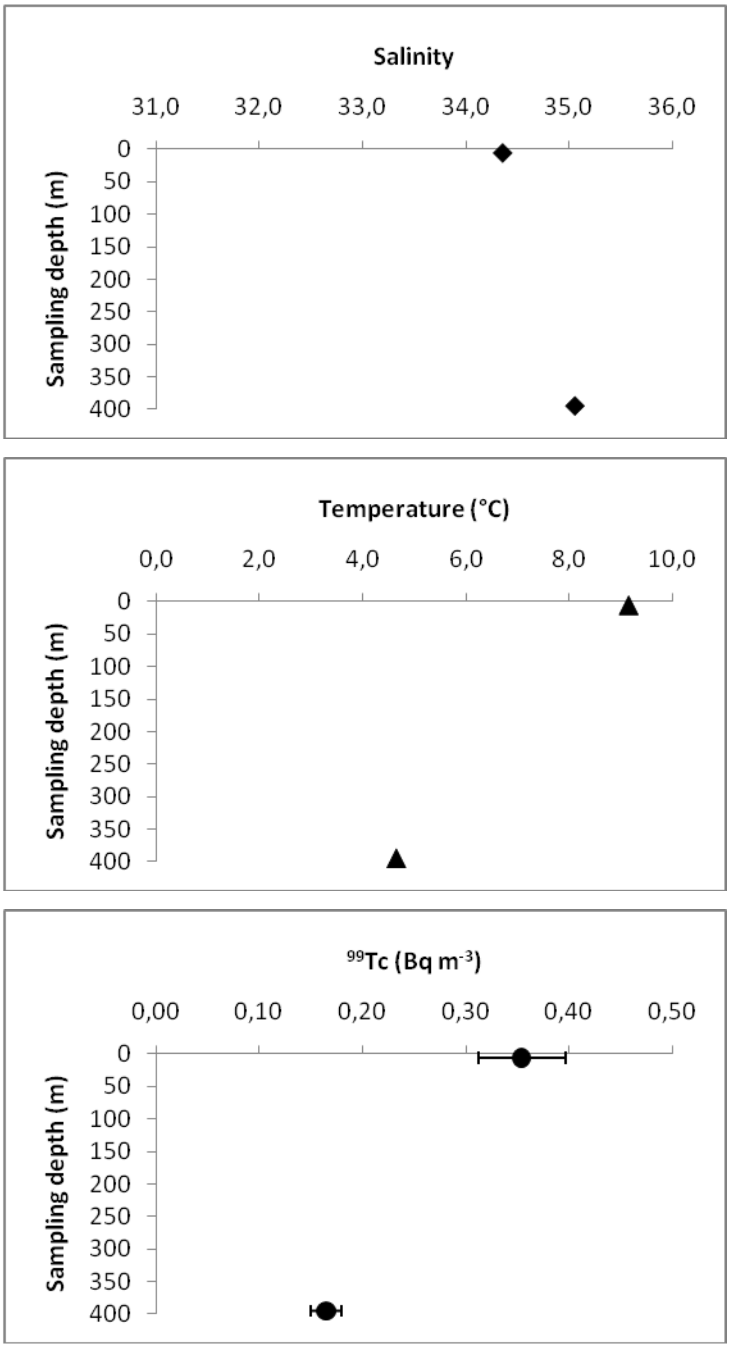


Figure 4.4: ^{99}Tc (Bq m^{-3}) in surface and bottom samples at sampling location Station 404 (71.25 N, 28.73 E) in the Barents Sea / NwCC in 2008 together with hydrographical data (salinity and temperature). (NRPA, 2011, Appendix 5)

At certain sampling locations in the Barents Sea in 2008 (e.g. st 417, see Appendix 5) the activity concentrations in the bottom sample (0.15 Bq m^{-3}) was similar to the concentration in surface sample (0.11 Bq m^{-3}). The slightly higher activity concentration in the bottom sample than in the surface sample is negligible when the uncertainties in the measurements are taken into account. From the hydrographical data in Appendix 5, it can be seen that the surface water (6 m) had a salinity of 34.97 and a temperature of 9.2 °C, while the bottom water (264 m) had salinity 35.03 and temperature of 4.6 °C.

In general, the ^{99}Tc activity concentration in the water column decreased, or showed no considerable difference with depth.

4.1.3 Transit times and transfer factors

Transit times (for definition, see page 23, chapter 1.4.2) from Sellafield to Norwegian waters have been estimated by several researchers. For example, Dahlgaard (1995) reported a transit time of 3-4 years to the NwCC and 5-6 years to the Barents Sea (based on distribution of radiocaesium from Sellafield). Following the enhanced discharges of ^{99}Tc from Sellafield in 1994, Brown et al. (1999) reported a transport time of about 2.5 years for EARP-related contamination to the Norwegian south-western coast. Brown et al. (2002) found a transit time of 3.5 years to the sampling location Hillesøy in Troms, the northern part of the NwCC.

Unfortunately, the present study consists of a data set with relatively low resolution, which makes calculations of transit times difficult. The peak ^{99}Tc activity concentration in seawater from the NwCC in 1999 (1.61 Bq m^{-3}) (see figure 3.19) is, however, probably due to the maximum discharge from Sellafield in 1995(~190 TBq/year), indicating a transport time of 4 years, consistent with the reported transport time for Sellafield radionuclides to the NwCC of 3-4 years (Dahlgaard, 1995, Brown et al., 2002). The peak in the seawater concentration in 2004 (figure 3.19) may be in response to the peak discharge in 2001 and 2002 (~80 TBq/year), indicating a transport time of approximately 2-3 years. This somewhat shorter transport time relative to the observation in 1999, could be explained by the fact that the two samples from 2004 were collected further south in the NwCC. When comparing this NwCC north of Stad time series from the present study (figure 3.19) with the NRPA Hillesøy time series (figure 1.8; NRPA (2009)), it can be seen that the maximum concentration were observed in 1999 in both time series. The Hillesøy time series has a considerably greater resolution than the time series in the present study. This is because Hillesøy seawater samples are taken at a fixed location and averages are based on monthly sampling. A decrease in activity concentrations can be seen in both time series.

Dahlgaard et al. (1995) reported an indicated transport time of 14-17 years from Sellafield to the North Atlantic Current. In 2010, 16 years had gone since the operation of EARP at Sellafield began in 1994. ^{99}Tc originating from the early EARP-pulse may therefore have reached the North Atlantic Current by 2010, assuming a transport time of 14-17 years. Thus, small fractions of old Sellafield ^{99}Tc discharges in the NAC may have influenced the ^{99}Tc activity concentrations measured in the North Sea in 2010, 2009 and 2008.

There are many uncertainties connected with transit time estimates. The transport time to a specific location is not well defined because the measured activity concentration will consist of variable fractions of past discharges and there are also temporal variations in transport time due to meteorological conditions (Dahlgaard, 1995).

Transfer factors (unit: Bq m^{-3} / PBq yr^{-1}, for definition see page 24, chapter 1.4.2) have been used to represent the degree of dilution of a tracer signal following transport from a well defined point-source (e.g. Kershaw et al., 2004). Estimated TFs from Sellafield to Værlandet are given in table 4.3. The TFs for ^{99}Tc from Sellafield to Værlandet were in the range of 10-23 Bq m^{-3} / PBq yr^{-1} in the years 2003 to 2006 (table 4.3). In 2008 and 2009 the TFs were higher, 71 and 77 Bq m^{-3} / PBq yr^{-1}, respectively. The latter is due to relatively high seawater concentrations at Værlandet and very low discharges from Sellafield 3 years earlier (in 2005 and 2006). These TFs probably do not represent an equilibrated system. The seawater activity concentrations have decreased, but not in the same magnitude as discharges from Sellafield. Discharges in 2005 and 2006 were reduced by one order of magnitude compared to the levels of discharge in 2000, 2001 and 2003.

Table 4.3: Estimated transfer factors (TFs) from Sellafield to Værlandet, assuming a transit time of 3 years. Sellafield discharge data: RIFE 6, 7, 9, 11 and 12.

Sampling date Værlandet	**^{99}Tc (Bq m^{-3})**	**Year of Sellafield discharge (transit time Sellafield-Værlandet ~ 3 years)**	**^{99}Tc discharge Sellafield (PBq/year)**	**TF (Bq m^{-3}/ PBq yr^{-1})**
19.05.2003	1.01	2000	0.0444	23
01.12.2003	0.70	2000	0.0444	16
10.05.2004	0.76	2001	0.079	10
23.11.2006	0.62	2003	0.037	17
27.10.2008	0.48	2005	0.0067	71
16.11.2009	0.43	2006	0.00562	77

Kershaw et al. (2004) calculated TFs for ^{99}Tc in 1994, 1998, 1999 and 2000 at three locations in the Barents Sea / NwCC. For 1994 they reported a ^{99}Tc TF of 66 Bq m^{-3} / PBq yr^{-1} near Fugløya. The TFs had decreased to 4-10 Bq m^{-3} / PBq yr^{-1} in the period 1998-2000. The 1994 TF included ^{99}Tc discharges from both La Hague and Sellafield, while for the other years, only Sellafield discharges were included. The 2003, 2004 and 2006 TFs calculated at Værlandet in the present study (table 4.3) seems to be in agreement with the TFs calculated by Kershaw et al. (2004) at Fugløya in 1998-2000, while the 2008 and 2009 TFs at Værlandet seems to be in agreement with the pre-EARP TF (assuming that the TFs decrease somewhat northwards from Værlandet to Fugløya). However, the 1994 and 2008/2009 TFs cannot be compared directly due to the inclusion of La Hague releases in 1994.

4.1.4 ^{99}Tc/^{137}Cs ratio

Radionuclides like ^{99}Tc and ^{137}Cs are individually useful as tracers, but the ratios between radionuclides can be even more useful. Radionuclide ratios can be used to identify sources, identify water masses and estimate transit times. For example, since 1995 the ^{99}Tc/^{129}I ratio in the Irish Sea close to Sellafield has been 3-4 orders of magnitude higher than close to La Hague (Nies et al., 2009). Measuring this ratio in a seawater sample may thus give information about the origin of the water mass and the pollution. In this discussion, the ^{99}Tc/^{137}Cs ratio is chosen because IMR measures both these radionuclides in Norwegian waters.

Radionuclide ratios can be very different for different sources, which is advantageous for identifying sources. (A disadvantage in tracer studies, however, is that radionuclide ratios from these sources can vary over time). The ratios do not change with dilution (Yiou et al., 2002). The ^{99}Tc/^{137}Cs ratio in the fallout from the Chernobyl accident was approximately $1.5 \cdot 10^{-5}$ (Aarkrog et al., 1988, Salbu and Holm, 2005). In comparison, the ^{99}Tc/^{137}Cs *discharge* ratio was about 15 following the enhanced Sellafield EARP ^{99}Tc discharges in 1995/1996 (McCubbin et al., 2002). This makes the ^{99}Tc/^{137}Cs-ratio a sensitive parameter for the mixing of saline-poor, ^{137}Cs-rich water from the Baltic Sea with saline- and ^{99}Tc-rich North Sea waters (Lindahl et al., 2003). The ratio is strongly affected by the outflow of Chernobyl derived ^{137}Cs in the water from the Baltic Sea. The outflow of water from the Baltic Sea varies from year to year (e.g. NRPA, 2006, NRPA, 2007, NRPA, 2008, NRPA, 2009).

Figure 4.5 shows the ^{99}Tc/^{137}Cs ratios in the North Sea and Skagerrak in 2007 (data taken from NRPA, 2009). The ^{99}Tc/^{137}Cs ratio in Skagerrak (0.06) is much lower compared to the ratio in the North Sea, near the east coast of Scotland (0.30). The lower ratio in Skagerrak is due to outflow of ^{137}Cs-rich water from the Baltic Sea, while the higher ratios in the North Sea are due to higher ^{99}Tc levels.

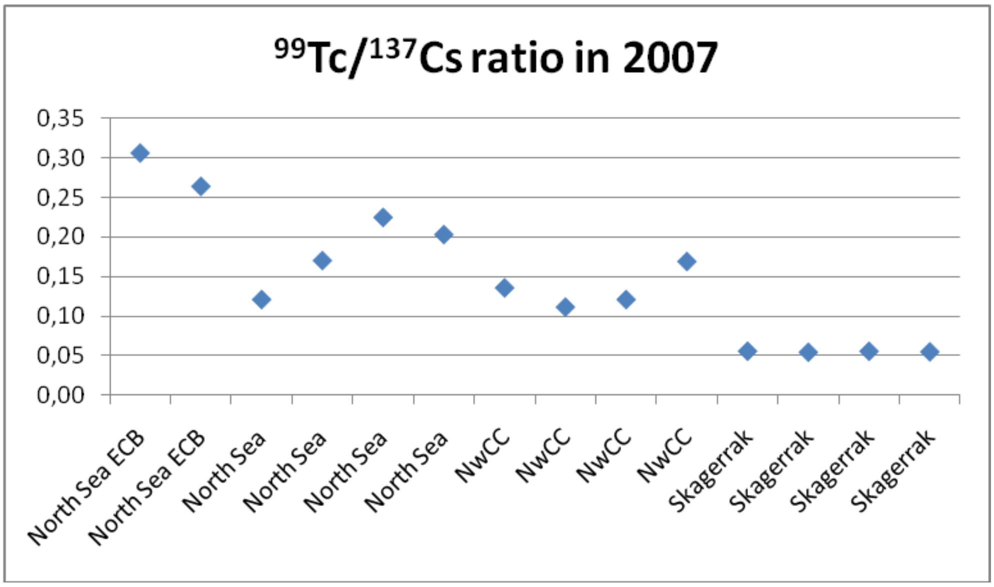


Figure 4.5: ^{99}Tc/^{137}Cs ratio in the North Sea and Skagerrak in 2007. Data from NRPA (2009).

Table 4.4 shows the ^{99}Tc/^{137}Cs ratio at the five “Tilførselsprogram”-stations in the North Sea in 2010. The lowest ratio (0.08) was observed at station T9, closest to the Skagerrak, where a relatively high ^{137}Cs activity concentration of 4.9 Bq m^{-3} was observed, due to outflow of Baltic water. The highest ratio was observed in the NwCC near Utsira where a ^{99}Tc activity concentration of 0.41 Bq m^{-3} (figure 3.1) was observed.

Table 4.4: ^{99}Tc/^{137}Cs ratios in the North Sea in 2010. ^{137}Cs-data: unpublished data from IAEA (data provided by Mats Eriksson via Hilde Elise Heldal), ^{99}Tc data: the present study

Station	**Lat**	**Long**	**^{137}Cs (Bq m^{-3})**	**^{99}Tc (Bq m^{-3})**	**^{99}Tc/^{137}Cs**
T9	57.78	7.11	4.9	0.40	0.08
T10	59.04	4.71	3.0	0.41	0.14
T11	59.02	3.85	3.1	0.35	0.11
T26	57.92	4.91	2.8	0.27	0.10
T27	60.83	1.33	2.0	0.20	0.10

Table 4.5 shows ^{99}Tc/^{137}Cs isotope ratios in surface waters from different areas and years. It is evident that enhanced values for ^{99}Tc and for the ^{99}Tc/^{137}Cs ratio were found in areas exposed to Sellafield discharges after EARP became operational in 1994. In the eastern part of the

Irish Sea, the observed radionuclide ratio was well above 1 in 1995, and also in some parts of the North Sea the ratio was above 1 in the following years (Salbu and Holm, 2005, McCubbin et al., 2002).

Table 4.5: Activity concentrations of ^{99}Tc and ^{137}Cs, and ^{99}Tc/^{137}Cs isotope ratios in surface waters from different areas and years (a selection of the most relevant literature data).

Year	**Area**	**^{99}Tc (Bq m^{-3})**	**^{137}Cs (Bq m^{-3})**	**^{99}Tc/^{137}Cs ratio**	**Data source**
1972	Irish Sea	108		0.036	(Salbu and Holm, 2005)
1995	E. Irish Sea	100-500		1-1.6	(Salbu and Holm, 2005)
1981	North Sea	3.5	175	0.02	(Salbu and Holm, 2005)
1996	North Sea	0.91-14	2.1-13	0.23-1.43	(McCubbin et al., 2002)
2007	North Sea (east coast Britain)	1.5	5	0.30	(NRPA, 2009)
2010	North Sea	0.33	3.16	0.11	(The present study, unpublished data IAEA)
1997	NwCC south of Stad	0.88-1.2	8.6-12	0.10	(McCubbin et al., 2002)
2007	NwCC south of Stad	0.58	4.4	0.13	(NRPA, 2009)
1983	Baltic Sea	0.07	14	0.005	(Salbu and Holm, 2005)
1986	Baltic Sea	0.04	200	0.0002	(Salbu and Holm, 2005)
2001	Swedish west coast	1.05 (average)		0.018-0.085*	(Lindahl et al., 2003)
2007	Skagerrak	0.52	9.3	0.06	(NRPA, 2009)

*The highest ratio in the north, lower in south near the entrance of the Baltic Sea.

It is also evident from Table 4.5 that the observed ^{99}Tc/^{137}Cs ratio became much lower in the Baltic Sea (decreasing from 0.005 to 0.0002) after the Chernobyl accident in 1986 (e.g. Salbu and Holm, 2005). This is due to the high level of cesium-137 in fallout over the Baltic Sea (HELCOM, 2011). Radioactive contamination can persist in the Baltic Sea for long periods due to the long residence time of the water in the Baltic Sea (25-35 years) (Matthäus and Schinke, 1999). The Chernobyl accident did not contribute significantly to the ^{99}Tc levels in the Baltic Sea or the North Atlantic (Aarkrog et al., 1988), since relatively small amounts of ^{99}Tc were released. Thus, the ^{99}Tc present in the Baltic Sea originates mainly from European nuclear reprocessing plants Sellafield (and La Hague) and global fallout. Aarkrog et al. (1988) estimated the transit time from Sellafield to the Baltic Proper to be 5-6 years. Due to dilution on its way from Sellafield, the ^{99}Tc activity concentration in the Baltic Sea is low (0.06 to

0.42 Bq m^{-3} in 2006 (The MARiS database (http://maris.iaea.org/), data provider: RISØ, Denmark).

4.2 Sinks for ^{99}Tc in the marine environment

4.2.1 Uptake in marine organisms

Radionuclides in seawater will be taken up, to varying extents, by marine organisms. The degree of biological uptake may be expressed by the "Concentration Factor" (CF) defined as the ratio between the activity concentrations in biota to the concentration in seawater (Bq kg^{-1} wet weight (w.w.) biota per Bq L^{-1} seawater) (IAEA, 2004). Uptake of ^{99}Tc in fish and other marine organisms is generally low, but some organisms, like brown seaweeds and lobster, exhibit a high uptake of ^{99}Tc. Table 4.6 contains CFs for selected marine organisms. In the literature, CFs for seaweeds is often calculated using dry weight (d.w.) basis. Sjøtun et al. (submitted for publication) reported dry weight / wet weight ratios of 0.24 and 0.16 for *F. vesiculosus* and *F. serratus*, respectively. Heldal and Sjøtun (2010) reported a dry weight/ wet weight ratio for *A. nodosum* of 0.28.

Table 4.6: Concentration factors (CFs) for lobster, other crustaceans, fish and brown seaweeds.

Specie	**CF** (Bq kg^{-1} w.w.) / (Bq L^{-1})	**Data source**
Lobster (tail muscle)	6850	(Smith et al., 2001)
Lobster	8000	(Brown et al., 1999)
Crustaceans	1000	(IAEA, 2004)
Fish	80	(IAEA, 2004)
Fish (edible flesh)	12	(Smith et al., 2001)
Seaweed:*CF calculated using dry weight (d.w.) basis.		
*Fucus vesiculosus**	$1.32 \cdot 10^5$	(Smith et al., 2001)
*Fucus vesiculosus**	$1.1 \cdot 10^5$	(Aarkrog et al., 1987)
Fucus vesiculosus	$3.9 \cdot 10^4$	(Sjøtun et al., Submitted for publication)
*Fucus serratus**	$1.21 \cdot 10^5$	(Brown et al., 1999)
Fucus serratus	$2.3 \cdot 10^4$	(Sjøtun et al., Submitted for publication)
*Ascophyllum nodosum**	$1.78 \cdot 10^5$	Holm et al. (1984) referred to in Salbu and Holm (2005)

4.2.1.1 Seaweeds and lobsters

^{99}Tc in brown seaweeds

Norway has a long coastline and approximately 10 000 km^2 of the coastal zone are covered with brown seaweed (Steen, 2009). Brown seaweed is a useful bioindicator of ^{99}Tc in the marine environment because it is easy accessible, widely distributed and has a high uptake of ^{99}Tc from seawater (NRPA, 2009). Bioindicators are defined as living organisms that quickly respond to changes in concentrations of different pollutants in the environment (IFE, 2011). Technetium has high concentration factors (CFs) in brown algae like *Ascophyllum nodosum, Fucus vesiculosus* and *Fucus serratus* (CFs $\approx 1\cdot10^5$ (unit: L kg^{-1}), dry weight basis) which makes detection possible even at low concentrations in seawater (Kershaw et al., 1999). Especially *F. vesiculosus* have been used as a bioindicator for ^{99}Tc in many studies (e.g. (Aarkrog et al., 1986, Aarkrog et al., 1987, Lindahl et al., 2003). Since 1986, The Institute for Energy Technology in Norway (IFE) have performed monthly sampling of *F. vesiculosus* from the coastal station Utsira in the south-western part of Norway (IFE, 2011, Christensen et al., 2001). In 1999/2000 a peak ^{99}Tc activity concentration of approximately 400 Bq kg-1 (dry weight) in *F. vesiculosus* was observed at this station (NRPA, 2009). This peak was the response of the maximum discharge from Sellafield 3-4 years earlier. The levels of ^{99}Tc in *F. vesiculosus* at Utsira and other coastal stations are now generally decreasing due to reduced discharges from Sellafield (NRPA, 2009). In 2008 and 2009, the average ^{99}Tc activity concentrations in this species from monthly sampling at Utsira were 99 and 89 Bq kg^{-1} d.w, respectively (NRPA, 2011). Using the ^{99}Tc seawater activity concentration near Utsira of 0.41 Bq m^{-3} in July 2010 (the present study), and assuming a CF of 10^5 (dry weight basis) for *F. vesiculosus,* the estimated activity concentration in this specie becomes approximately 41 Bq kg^{-1} (d.w). This is in very good agreement with the observed activity concentrations of ^{99}Tc in *F. vesiculosus* in July/August 2010 (IFE: E. Strålberg, pers. comm. See table 4.7 below). From table 4.7 it can be seen that activity concentrations were somewhat higher during spring (May) and autumn (September) than in the summer months. The lower ^{99}Tc activity concentrations in *Fucus* during summer may be caused by lower ^{99}Tc seawater activity concentrations due to large amounts of freshwater run-off from land. Another possible explanation for this seasonal effect could be due to greater growth rate of seaweed during summer, causing a “dilution effect” (Heldal and Sjøtun, 2010).

Table 4.7: ^{99}Tc activity concentrations in *Fucus vesiculosus* from Utsira (summer 2010). The uncertainty is given as 1 standard deviation of the observed concentrations.

Sampling date	**^{99}Tc [Bq kg^{-1} dry weight]**	**Data source**
11.05.2010	104 ± 3	IFE, (E. Strålberg, pers. comm.)
14.06.2010	57 ± 2	“
12.07.2010	39 ± 2	“
19.08.2010	41 ± 2	“
16.09.2010	71 ± 2	“

Considering the high CFs for ^{99}Tc in these species (table 4.6), it is reasonable to assume that considerable amounts of ^{99}Tc may have accumulated in brown seaweeds along the Norwegian coast. The estimated total amount of *Ascophyllum nodosum* is approximately 1.8 million tonnes (Steen, 2008). The corresponding amount of *Laminaria hyperborea* along the Norwegian coastline is 50 million tonnes (Steen, 2009).

The ^{99}Tc CF for A. *nodosum* of $1.78 \cdot 10^5$ (Bq kg^{-1} d.w.)/(Bq L^{-1}) given in Salbu and Holm (2005) can be converted to wet weight basis using the dry weight/ wet weight ratio for *A. nodosum* of 0.28 reported by Heldal and Sjøtun (2010), giving a CF of $5 \cdot 10^4$ (Bq kg^{-1} w.w.)/(Bq L^{-1}). The average annual ^{99}Tc activity concentrations in *A. nodosum* at Utsira in 2007, 2008 and 2009 were approximately 100 Bq kg^{-1} (dry weight) ≈ 28 Bq kg^{-1} (wet weight) (NRPA, 2009; NRPA, 2011). This activity concentration of 28 Bq kg^{-1} (wet weight) corresponds to a seawater concentration of 0.56 Bq m^{-3} at Utsira, assuming a constant CF of $5 \cdot 10^4$ L kg^{-1} under equilibrium conditions. This is in very good agreement with the measured seawater activity concentration in this area in 2007, see figure 3.8. The use of CF assumes that organisms are in equilibrium with their surrounding seawater with respect to element concentrations, and rates of uptake and release of the radionuclide are not taken into account (IAEA, 2004).

Using the estimated amount of *A. nodosum* along the Norwegian coast of $1.8 \cdot 10^9$ kg, and assuming that an activity concentration of 28 Bq kg^{-1} at Utsira is representative for the entire Norwegian coast line, the total amount of ^{99}Tc “stored” in *A. nodosum* along the Norwegian coast becomes $5.04 \cdot 10^{10}$ Bq, or 0.05 TBq. This amounts to 0.006 % of the total ^{99}Tc discharges from Sellafield in the period 1994-2004. However, the activity concentration of ^{99}Tc in *A. nodosum* in the northern part of the Norwegian coast is probably somewhat lower than at Utsira. Therefore, the amount of ^{99}Tc stored in this specie may be overestimated. On the other hand, ^{99}Tc is also accumulated by other brown seaweed species (e.g. *F. vesiculosus*). Thus, the total amount of ^{99}Tc stored in brown seaweeds along the Norwegian coast is probably greater than 0.05 TBq.

Using the CF of $5 \cdot 10^4$ (Bq kg^{-1} w.w.)/(Bq L^{-1}), the present ^{99}Tc activity concentrations in the NwCC presented in this study (~0.34 Bq m^{-3} in 2010), would give a low activity concentration in *A. nodosum*; approximately 17 Bq kg^{-1} (w.w.). The ^{99}Tc activity concentration in seawater must be more than 20 Bq m^{-3} for the concentration in *A. nodosum* to exceed 1000 Bq kg^{-1} (w.w.). A ^{99}Tc activity concentration of ~20 Bq m^{-3} in the south-western part of the NwCC, corresponds to a discharge of ~1000 TBq y^{-1} approximately 3 years earlier. (Assuming a transit time of 3 years and a TF of 20 Bq m-3 / PBq y^{-1} estimated by Brown et al. (1999)). This is a very unlikely scenario.

^{99}Tc in lobsters

For crustaceans, the highest levels of ^{99}Tc are found in lobsters. Brown et al. (1999) measured ^{99}Tc activity concentrations in lobsters ranging from 11.2 to 42 Bq kg^{-1} w.w along the southern coast of Norway during the autumn in 1997. In the same study, a CF of 8000 for lobster claw muscle was reported (table 4.6). In comparison, Smith et al. (2001) reported a mean annual ^{99}Tc activity concentration of 237 Bq kg^{-1} w.w. in lobster (tail muscle) from the western Irish Sea the same year. They estimated a CF of 6850 (table 4.6) for lobster tail muscle collected in 1997 and 1998, similar to the value of Brown et al. (1999). The lower seawater ^{99}Tc activity concentrations in Norwegian Coastal waters compared to the Irish Sea, naturally gave lower ^{99}Tc levels in lobsters from Norwegian waters. The uptake of ^{99}Tc in other crustaceans is lower (e.g. Smith et al., 2001). IAEA (2004) stated that a higher value than the recommended CF of 1000 for crustaceans should be applied for lobster. Female lobsters exhibit a significantly larger uptake of ^{99}Tc than male lobsters (e.g. NRPA 2008). At present, the reason for this seems to be unknown.

The present ^{99}Tc activity concentrations in the NwCC (~0.34 Bq m^{-3}) would give low activity concentrations in lobster. Assuming a CF of 8000 (Brown et al., 1999), the estimated concentration in lobster is 2.72 Bq kg^{-1} (w.w.). The ^{99}Tc activity concentration in seawater must be more than 125 Bq m^{-3} for the concentration in lobster to exceed 1000 Bq kg^{-1} (w.w.) (assuming a CF of 8000). A ^{99}Tc activity concentration of ~125 Bq m^{-3} in the south-western part of the NwCC, corresponds to a discharge of ~6250 TBq y^{-1} approximately 3 years earlier. (Assuming a transit time of 3 years and a TF of 20 Bq m-3 / PBq y^{-1} estimated by Brown et al. (1999)). This is an extremely unlikely scenario.

4.2.1.2 Uptake in other marine organisms

By contrast to brown seaweeds and lobsters, uptake of ^{99}Tc in fish and other marine organisms is low. Smith et al. (2001) reported a CF of 12 (fish filet), while IAEA (2004) recommends a value of 80 (all parts of the fish is taken into account) (table 4.6).

Heldal et al. (2004) reported low levels of ^{99}Tc (0.11 and 0.19 Bq kg^{-1} wet weight) in two samples of wolfish (*Anarhichas sp.*) collected at Kalvåg (Sogn og Fjordane) in 2003 (Heldal et al., 2004). These levels are more than 8000 times below the EU recommended maximum permitted level of ^{99}Tc in seafood of 1250 Bq kg^{-1} (wet weight), to be applied during any future nuclear accident (Brown et al., 1998).

^{99}Tc has a very low dose factor (effective dose equivalent) of 6.4 x 10^{-10} Sv/Bq (ICRP, in Nies et al., 2000, Nies et al., 2009). This is considerably lower than ^{137}Cs which has a dose factor of 1.4 x10^{-8} Sv/Bq (Nies et al., 2000, Nies et al., 2009). Smith et al. (2001) concluded that the mean annual doses to typical and heavy consumers of seafood from the Irish Sea in the period 1996-1998 was 0.0061 µSv and 0.24 µSv, respectively. These doses are of negligible radiological significance compared to the annual dose limit of 1 mSv (1000 µSv) (ICRP, 2007) for members of the public.

Because the levels of ^{99}Tc in Norwegian marine waters and ecosystems are much lower than in the Irish Sea, doses from consuming fish or shellfish from Norwegian waters does not represent an obvious health hazard. Nevertheless, there are large uncertainties concerning the effects in biota from exposure to low levels of radioactivity, and long-term effects in the marine ecosystem should not be ignored (UMB, 2009, AMAP, 2010). Norway is a large fishery nation, and the fishing industry as well as the public is concerned when it comes to radioactive contamination. Therefore, monitoring of ^{99}Tc and other radionuclides in Norwegian marine waters is important in order to document the concentration levels and trends.

4.2.2 Binding of ^{99}Tc in sediments

Radionuclides are transferred from the water column to the sediments by scavenging processes, making the sediments a sink for some radionuclides. Physical mixing by currents and/or bioturbation (mixing of sediments by marine organisms) may later on lead to oxidation of species originally present in reduced form in sediments, causing remobilisation of buried radionuclides from the sediment to the water column.

^{99}Tc is redox reactive, i.e. it can exist in different chemical forms. Technetium-99 is released in effluents as the highly soluble pertechnetate ($^{99}TcO_4^-$). Under anoxic conditions, however, $Tc(VII)O_4^-$ is reduced to particle reactive Tc(IV) species. Such anoxic conditions are found in the fine-grained sediments of the Irish Sea (Finegan et al., 2009), and retention of ^{99}Tc in these sediments is therefore expected. Several studies (e.g. (McCubbin et al., 2002, Leonard et al., 2004, McCubbin et al., 2006, Finegan et al., 2009) have confirmed that substantial amounts of ^{99}Tc have accumulated in the sediments in the Irish Sea. Remobilization may therefore act as a secondary source of ^{99}Tc in the future. Remobilisation of ^{137}Cs from sediments contaminated by the large Sellafield-discharges during the 1970s is actually now the main source term (about 90 %) of this radionuclide to the Irish Sea (e.g. McCubbin et al., 2002, Leonard et al., 2004).

Leonard et al. (2004) concluded that the Irish Sea sediments may provide a future source of ^{99}Tc to the water column if the discharges from Sellafield become zero or greatly reduced. The discharges are now greatly reduced (the discharge in 2009 was less than 2% of the peak discharge in 1995 (RIFE-1, 1996, RIFE-15, 2010). Despite this great reduction in discharges, Finegan et al. (2009) considered it likely that the sediments of the Irish Sea will continue to retain the accumulated technetium for many decades to come, and that remobilisation of ^{99}Tc from the sediments will happen at a slower rate than for ^{137}Cs. The slow redissolution of ^{99}Tc makes it reasonable to believe that future levels of this radionuclide in local seafood will be small, but measurable, and that contamination will be present for decades to come (McCubbin et al., 2006). Finegan et al. (2009) estimated that as much as approximately 20% of the total ^{99}Tc discharges from Sellafield may have been retained in the fine-grained subtidal sediments of the eastern Irish Sea.

Little is known about accumulation of ^{99}Tc in sediments along the Norwegian coast. The near-shore sediments of many coastal systems are anoxic and some Scandinavian fjords have anoxic conditions (Keith-Roach and Roos, 2004). In the event that ^{99}Tc is in fact not behaving as conservatively as previously thought, it can be assumed that a portion of the ^{99}Tc originating from Sellafield have been vertically transported from the water column into sediments along the Norwegian coast. This has been briefly discussed by Brown et al. (2002). They reported a lower transfer factor (6 Bq m^{-3} per PBq y^{-1}) from Sellafield to northern Norway (with a transport time of approximately 3.5 years), than transfer factors reported in other studies (e.g. Dahlgaard (1995) reported TFs in the range 10-50 Bq m^{-3} per PBq y^{-1} for a conservative radionuclide). Assuming that the transfer factors from Sellafield to Arctic waters were in fact lower than those previously estimated, Brown et al. (2002) suggested the possibility that a larger proportion of ^{99}Tc than that expected for a conservative tracer, is removed from the water column on its transport route from Sellafield to northern Norwegian waters through interaction with more reducing environments than the oxic surface waters of the open North Sea.

In 1999 and 2000, Keith-Roach and Roos (2004) investigated the behaviour of ^{99}Tc in the Framvarden fjord, which is a highly stratified, anoxic (highly sulphidic) fjord located in southern Norway. As expected, they found that conservative behaving $^{99}TcO_4^-$ entering the fjord is reduced to Tc(IV) below the redox-cline and high K_d values were observed. Although the largest fraction of ^{99}Tc was associated with particles (41%) and colloids (20%), as much as 39% was present as ”soluble” $^{99}Tc(IV)$ complexes in this strongly reducing environment. The particle-bound ^{99}Tc was found to settle effectively to the sediments, while the colloidal and ”soluble” Tc complexes migrated much more slowly. The maximum concentration of ^{99}Tc in the sediments of Framvarden corresponded to the peak Sellafield discharge in 1978, which arrived in Framvarden 4 years later (1982). At the time of sampling, the recent peak emissions from Sellafield following EARP had not yet reached the sediments. The observations by Keith-Roach and Roos (2004) confirm that sediments may act as a sink for ^{99}Tc. The Framvarden fjord is not representative of most Norwegian fjord systems. However, it is possible that a small amount of ^{99}Tc may be retained in reducing sediments high in organic matter in Norwegian coastal areas and fjords. In order to investigate this, further research is required.

4.3 The OSPAR Commission and their work concerning radioactive substances

The OSPAR Convention (The Convention for the Protection of the marine Environment of the North-East Atlantic) is a continuation of two earlier conventions (the Oslo Convention and the Paris convention) and entered into force in 1998 (OSPAR, 2011). The OSPAR commission is the forum through which the fifteen member countries on the western coasts of Europe cooperate to protect the marine environment of the North-East Atlantic. OSPAR countries work on radioactive substances has focused on reducing discharges from the nuclear sector.

The OSPAR Strategy objectives for radioactive substances are to:

- ✓ Prevent pollution of the maritime area from ionising radiation through progressive and substantial reductions of discharges, emissions and losses of radioactive substances.
- ✓ Reduce by 2020 discharges, emissions and losses of radioactive substances to levels where the additional concentrations in the marine environment above historic levels, resulting from such discharges, emissions and losses, are close to zero.
- ✓ The ultimate aim is of concentrations in the environment near background values for naturally occurring radioactive substances and close to zero for artificial radioactive substances. In achieving this objective, the legitimate uses of the sea, technical feasibility, and radiological impacts on man and biota should be taken into account. (OSPAR, 2010b)

OSPAR have focused especially on the ^{99}Tc discharges from the nuclear reprocessing sector (Sellafield). In a report from the OSPAR Commission in 2009, (OSPAR, 2009b) progress towards the OSPAR objectives on concentrations of radioactive substances in the marine environment was evaluated. The OSPAR maritime regions was divided into 15 monitoring areas reflecting ocean circulation patterns and the location of nuclear sources, and the mean activity concentrations of indicator radionuclides in seawater, seaweed and marine organisms in the assessment period (2002-2006) was compared with mean concentrations for the baseline period (1995-2001). For ^{99}Tc, only seawater and seaweed activity concentrations were evaluated. Of the cases where enough data to allow statistical tests to be performed was available, there were either no change or a reduction in the levels of ^{99}Tc between the assessment and baseline period. The results in the present study are in good agreement with the OSPAR-results (although no statistical tests were used in the present study).

The OSPAR countries have succeeded in reducing releases of radionuclides to the marine environment. In their 2010 quality status report, OSPAR reported that discharges of beta-activity have decreased by 38 % since the period 1995-2001 (OSPAR, 2010b). The reduction in discharges of ^{99}Tc from Sellafield is a major reason for this positive trend. The reduction of ^{99}Tc discharges have also led to reduction in discharges of other radionuclides such as ^{90}Sr and ^{137}Cs since the MAC waste also was a significant source of these radionuclides (OSPAR, 2009b). As a result of the reduction in discharges from Sellafield during recent years, OSPAR now consider this radionuclide to be of reducing importance of the radionuclide discharges from the marine environment (OSPAR, 2009b).

Is it realistic that activity concentrations of ^{99}Tc, above historic levels, will be close to zero by 2020? When will ^{99}Tc levels in Norwegian coastal waters be “close to zero”? Assuming that the discharges from Sellafield and La Hague and other sources continues at a very low level, activity concentrations in seawater and biota will decrease further. A very simplistic way to evaluate when seawater activity concentrations will be close to zero, is to make a linear regression line through the data points in the trend diagram for the NwCC south of Stad (figure 4.6). If the trend continues as predicted by a linear model, concentrations will be close to zero in 2018. However, it is unlikely that activity concentrations will ever reach zero (the ‘fallout background level’ is, as mentioned earlier, reported to be 0.005 Bq m^{-3} (Dahlgaard et al., 1995)). An exponential trend line in figure 4.6 (red) is used to represent this scenario. ^{99}Tc has a long half life and will be present in the marine environment in the unforeseeable future. Old discharges will continue to circulate in the oceans for decades to come.

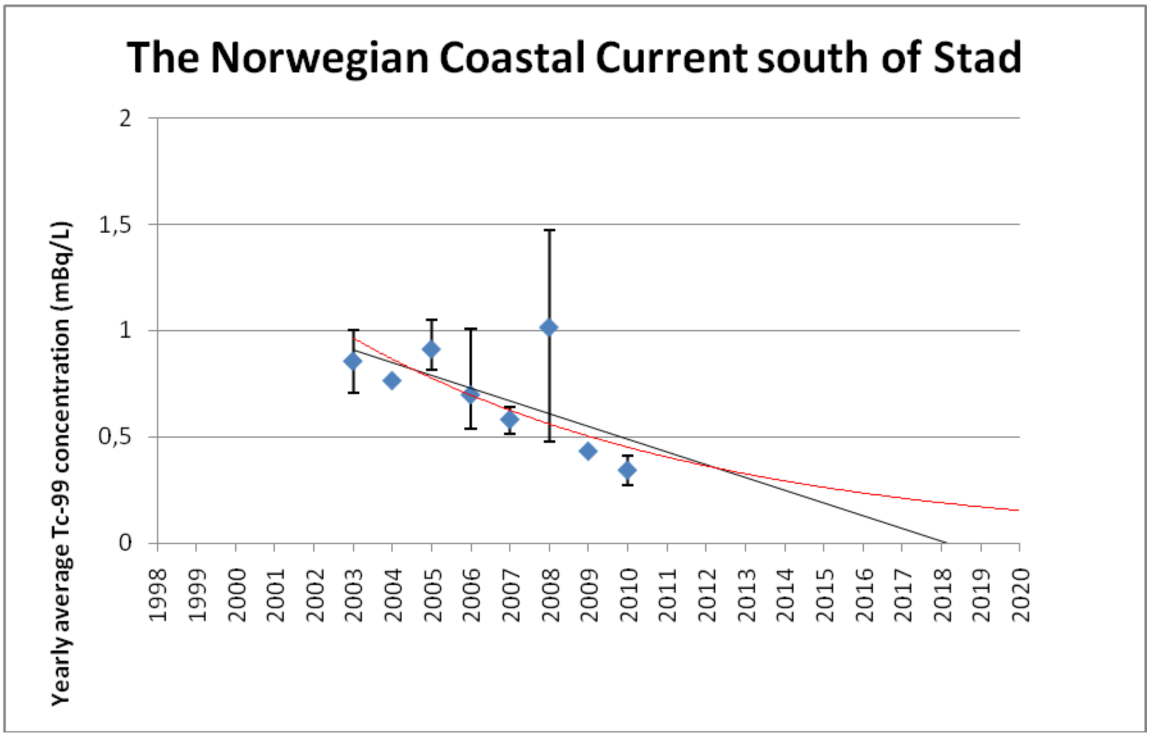


Figure 4.6: Time-series of ^{99}Tc activity concentrations (Bq m^{-3}) in the NwCC south of Stad with a linear (black) and an exponential (red) trend line.

4.4 The risk of accidents at the Sellafield site

Large, uncontrolled liquid releases of ^{99}Tc from Sellafield to the Irish Sea is now unlikely, since all of the stored the Medium Active Concentrate have already been treated in EARP, and the main part of newly formed ^{99}Tc is vitrificated and stored as solid waste on land (OSPAR, 2009).

The greatest potential risk at Sellafield is an accident with atmospheric release of radionuclides. NRPA recently published a report on the environmental consequences in Norway from an hypothetical accident at Sellafield, focusing on the effects from ^{137}Cs fallout (Thørring et al., 2010). With wind direction towards Norway, the western-part of Norway would be greatly affected by fallout from such an accident. The fallout from a Sellafield accident would give 7 times more fallout of ^{137}Cs than after the 1986 Chernobyl accident.

Atmospheric transport is much more rapid than transport by ocean currents. It would only take some hours (Ytre-Eide et al., 2009) for radioactive fallout to reach western-Norway. By contrast, it took 2.5 years for ^{99}Tc to reach the Norwegian coast after the elevated discharges in 1994.

4.5 Evaluation of the analytical method

4.5.1 Yield monitor

The analytical method for determination of ^{99}Tc in environmental samples requires the use of a yield monitor in order to determine possible losses during the radiochemical separation. The use of several isotopes of technetium as tracers has been described in the literature; ^{99m}Tc ($t_{1/2}$ = 6.02 hours) e.g. (Dowdall et al., 2004), ^{97}Tc ($t_{1/2} = 2.6 \cdot 10^6$ years) e.g. (Anderson and Walker, 1980), ^{97m}Tc ($t_{1/2}$ = 90 days) e.g. (Kaye et al., 1982), and ^{95m}Tc ($t_{1/2}$ = 61 days). However, IMR uses rhenium (Re), a stable analogue of Tc, as a non-isotopic carrier and yield monitor. An advantage with the use of Re, is that it is convenient to use aboard ship as pre-concentration can take place immediately after adding the Re-tracer. (Since Re is stable, there is no need to worry about decay of the yield monitor). Pre-concentration aboard the ship is advantageous because it is much easier to store and transport the anion exchange columns (50 ml syringes), compared to bringing back hundreds of litres of seawater in carboys to the laboratory. There are also some problems in using such a non-isotopic yield monitor, compared to isotopes of technetium. The problems arise from the slight difference in chemical properties of Tc and Re. Differences exist in the anion exchange behaviour, volatility and redox behaviour between the two elements. However, the method of analysis used by IMR, based upon Harvey et al. (1991, 1992), does take the differences in chemical properties between Tc and Re into account, and Re has proved successful as a yield monitor.

4.5.2 Radiometric vs. mass spectrometric methods for determination of ^{99}Tc in environmental samples

Radiometric methods using GM counters or liquid scintillation are the dominating analytical techniques used for determination of ^{99}Tc in environmental samples. In these methods the decay rate of technetium-99 is measured. The radiometric methods require a chemical separation of Tc from the matrix and from interfering radionuclides. Large samples are usually required due to the low concentrations of ^{99}Tc in the environment. The chemical separation is therefore not only important in order to separate Tc from other radionuclides, but also to gain a high chemical recovery of ^{99}Tc (Hou and Roos, 2008). However, during the last decades, more sensitive methods using mass spectrometric methods have been developed for the determination of trace levels of ^{99}Tc in environmental samples (Salbu and Holm, 2005). In mass spectrometry the measurements are based on the mass-to-charge ratio of charged particles. For quantitative measurements, the number of atoms of the radionuclide of interest (or the concentration) in a sample is directly measured. Mass spectrometric methods are sensitive methods for the determination of ^{99}Tc due to its long half-life, 2.1 x 10^5 y, and low specific activity, 6.3 x 10^8 Bq g^{-1}(Hou and Roos, 2008). Examples of mass spectrometric methods used for the determination of ^{99}Tc are inductively coupled plasma mass spectrometry (ICP-MS), accelerator mass spectrometry (AMS) and thermal ionization mass spectrometry TIMS (Hou and Roos, 2008).

During recent years, ICP-MS has become widely used for the determination of ^{99}Tc (Mas et al., 2004, Salbu and Holm, 2005). The challenge with this method is the potential interfering species on mass 99, for example from ^{99}Mo and the stable isotope ^{99}Ru. Radiochemical separation in order to remove these interfering species is performed using ion chromatography, with ^{99m}Tc as a yield monitor (Salbu and Holm 2005). The disadvantage with ^{99m}Tc as a yield monitor is the risk that some ^{99}Tc will be present in the tracer due to the fact that ^{99}Mo disintegrates to both the meta stable ^{99m}Tc and ^{99}Tc in the generator providing ^{99m}Tc (^{99}Mo – ^{99m}Tc generator / “Tc-cow”). This problem can be accounted for using an analytical blank.

The detection limits are generally improved (lowered) using modern mass spectrometric methods such as ICP-MS and AMS compared to traditional GM counters. The detection limit using an anti-coincidence shielded gas-flow GM counter is typically between 1-5 mBq, while detection limits using ICP-MS and AMS are typically between 0.01-15 mBq and 0.005-0.010 mBq, respectively (Salbu and Holm, 2005). The detection limit for ICP-MS depends on several factors such as the mass analyzer (e.g. quadrupole) and sample introduction system. The sample introduction technique electro thermal vaporization (ETV) has been used to remove Ru and Mo (Salbu and Holm, 2005).

Another advantage with methods like ICP-MS and AMS are the short separation and counting time compared to radiometric methods. In the present work the separation time was 7 days and the counting time using the GM counter was 48 hours. With ICP-MS and AMS the separation time is 1-2 days and the count time is approximately 30 minutes (Hou and Roos, 2008).

Today, radiometric methods are still dominating due to well controlled blank counts and inexpensive equipment (Hou and Roos, 2008). However, the use of mass spectrometric methods such as ICP-MS is becoming increasing popular in the determination of ^{99}Tc in environmental samples.

5. Conclusions

The results from this study show that the reduction in the ^{99}Tc discharges from Sellafield in 2003/2004, partly due to pressure from the Norwegian government, has caused a decrease in the seawater levels of this radionuclide in the North and Nordic Seas during recent years. The observed mean ^{99}Tc activity concentration in the northern North Sea and Norwegian coastal waters in 2010 (0.33 Bq m^{-3}) were ten times lower than the mean level observed by the NRPA in 1999. The ^{99}Tc activity concentrations in the Norwegian and Barents Sea have generally been at a constant, relatively low level during the last decade. However, the levels in the North Sea off the Scottish coast (0.77 Bq m^{-3}) are still significantly higher today than before 1994. Further, the present levels are much higher than the 'fallout background level' of 0.005 Bq m^{-3} reported for oceanic Atlantic water (Dahlgaard et al., 1995).

^{99}Tc activity concentrations are higher in the Norwegian Coastal Current (salinity <34.8) than in open sea areas with high influence of Atlantic water (salinity >35), reflecting ocean current patterns. Surface seawater samples generally have higher ^{99}Tc activity concentrations than samples collected in the water column or near the bottom.

Due to the relatively low spatial and temporal resolution of the data set, it was difficult to make calculations of transit times and transfer factors of ^{99}Tc from Sellafield to Norwegian waters. However, the 1999 peak in the time series from the Norwegian coastal current north of Stad indicated a transit time of 4 years to this area, consistent with literature data (Dahlgaard, 1995, Brown et al., 2002).

Because of the reduction in discharges from Sellafield, seawater activity concentrations of ^{99}Tc in the North and Nordic Seas are expected to decrease further. However, due to its long half-life (213 000 years), ^{99}Tc will be present in the marine environment in the unforeseeable future, and trace levels in environmental samples will probably be measured for decades to come. Norway is one of the world's leading seafood exporting nations, and any rumours on radioactive contamination in the marine environment may have a negative impact on the seafood industry. Further monitoring of the levels of radioactivity in seawater and marine organisms is therefore important, in order to ensure that fish and seafood from Norwegian waters are caught in clean waters.

Suggestions for further work:

- To compare the observed environmental ^{99}Tc activity concentrations with results from the oceanographic model ROMS in order to validate this model.
- Continue to monitor levels of ^{99}Tc in the North and Nordic Seas, but perhaps take fewer samples and concentrate on fixed stations in order to better evaluate trends.

References

AMAP (2010) AMAP Assessment 2009: Radioactivity in the Arctic. Oslo, Norway, Arctic Monitoring and Assessment Programme (AMAP).

AMUNDSEN, I., BREKKEN, A. & LILAND, A. (2003) Discharges of radioactive substances from the Sellafield site. Examination of British authorities' proposals for discharge authorisation at the Sellafield site. *StrålevernRapport 2003:2.* Østerås, Norwegian Radiation Protection Authority. Language: Norwegian.

ANDERSON, T. J. & WALKER, R. L. (1980) DETERMINATION OF PICOGRAM AMOUNTS OF TC-99 BY RESIN BEAD MASS-SPECTROMETRIC ISOTOPE-DILUTION. *Analytical Chemistry,* 52**,** 709-713.

BEASLEY, T. M. & LORZ, H. V. (1986) A review of the biological and geochemical behaviour of technetium in the marine environment. *Journal of Environmental Radioactivity,* 3**,** 1-22.

BROWN, J., KOLSTAD, A. K., LIND, B., RUDJORD, A. L. & STRAND, P. (1998) Technetium-99 Contamination in the North Sea and in Norwegian Coastal Areas 1996 and 1997. *StrålevernRapport 1998:3.* Østerås, Norwegian Radiation Protection Authority.

BROWN, J. E., IOSPJE, M., KOLSTAD, K. E., LIND, B., RUDJORD, A. L. & STRAND, P. (2002) Temporal trends for Tc-99 in Norwegian coastal environments and spatial distribution in the Barents Sea. *Journal of Environmental Radioactivity,* 60**,** 49-60.

BROWN, J. E., KOLSTAD, A. K., BRUNGOT, A. L., LIND, B., RUDJORD, A. L., STRAND, P. & FOYN, L. (1999) Levels of Tc-99 in seawater and biota samples from Norwegian coastal waters and adjacent seas. *Marine Pollution Bulletin,* 38**,** 560-571.

BRUNGOT, A. L., FØYN, L., CARROLL, J., KOLSTAD, A. K., BROWN, J., RUDJORD, A. L., BØE, B. & HELLSTRØM, T. (1999) Radioactivity in the marine environment. Report from the national surveillance programme. *StrålevernRapport 1999:6.* Østerås, Norwegian Radiation Protection Authority.

CHOPPIN, G. R., RYDBERG, J. & LILJENZIN, J. O. (2002) *Radiochemistry and nuclear chemistry,* [Oxford], Butterworth-Heinemann.

CHRISTENSEN, G. C., STRÅLBERG, E. & HOLM, E. (2001) Time trends of anthropogenic radionuclides at Utsira. *The Eight Nordic Seminar on Radioecology, 25-28 February 2001.* Rovaniemi, Finland, http://www.iaea.org/inis/collection/NCLCollectionStore/_Public/33/071/33071243.pdf .

DAHLGAARD, H. (1995) Transfer of European coastal pollution to the Arctic: Radioactive tracers. *Marine Pollution Bulletin,* 31**,** 3-7.

DAHLGAARD, H., CHEN, Q., HERRMANN, J., NIES, H., IBBETT, R. D. & KERSHAW, P. J. (1995) ON THE BACKGROUND LEVEL OF TC-99, SR-90 AND CS-137 IN THE NORTH-ATLANTIC. *Journal of Marine Systems,* 6**,** 571-578.

DOWDALL, M., GWYNN, J. P., SELNÆS, Ø. G. & LIND, B. (2003) Monitoring of 99Tc in the Norwegian Arctic marine environment. StrålevernRapport 2003:5. Østerås, Norwegian Radiation Protection Authority.

DOWDALL, M., SELNÆS, Ø. G., GWYNN, J. P. & LIND, B. (2004) On the Use of 99Mo/99mTc Generators in the Analysis of Low Levels of 99Tc in Environmental Samples by Radiochemical Methods. *Water, Air, and Soil Pollution,* 156**,** 287-297.

EHMANN, W. D. & VANCE, D. E. (1991) *Radiochemistry and nuclear methods of analysis,* John Wiley & Sons, Inc.

EML (1997) EML Procedures Manual, HASL-300, The Procedures Manual of the Environmental Measurements Laboratory, Section 4.5.3: Quality Control and Detection Limits, vol 1,. 28 ed.

FINEGAN, P., VINTRÓ, L. L., MITCHELL, P. I., BOUST, D., GOUZY, A., KERSHAW, P. J. & LUCEY, J. A. (2009) Accumulation, solid partitioning and remobilisation of 99Tc in subtidal and intertidal sediments in the Irish Sea. *Continental Shelf Research,* 29**,** 1995-2010.

GJØSÆTER, H., DOMMASNES, A., FALKENHAUG, T., HAUGE, M., JOHANNESEN, E., OLSEN, E. & SKAGSETH, Ø. (2009) Havets ressurser og miljø 2009. *Fisken og havet, særnr. 1-2009 (In Norwegian).*

HAIDVOGEL, D. B., ARANGO, H., BUDGELL, W. P., CORNUELLE, B. D., CURCHITSER, E., DI LORENZO, E., FENNEL, K., GEYER, W. R., HERMANN, A. J., LANEROLLE, L., LEVIN, J., MCWILLIAMS, J. C., MILLER, A. J., MOORE, A. M., POWELL, T. M., SHCHEPETKIN, A. F., SHERWOOD, C. R., SIGNELL, R. P., WARNER, J. C. & WILKIN, J. (2008) Ocean forecasting in terrain-following coordinates: Formulation and skill assessment of the Regional Ocean Modeling System. *Journal of Computational Physics,* 227**,** 3595-3624.

HARMS, I. H. & KARCHER, M. J. (2003) Pathways of anthropogenic radioactivity in the Northern Oceans. IN SCOTT, E. M. (Ed.) *Modelling Radioactivity in the Environment.* Elsevier Science.

HARVEY, B. R., IBBETT, R. D., WILLIAMS, K. J. & LOVETT, M. B. (1991) The determination of technetium-99 in environmental materials. *Aquatic Environment Protection: Analytical Methods, MAFF Directorate of Fisheries Research.* Lowestoft.

HARVEY, B. R., WILLIAMS, K. J., LOVETT, M. B. & IBBETT, R. D. (1992) Determination of technetium-99 in environmental material with rhenium as a yield monitor. *Journal of Radioanalytical and Nuclear Chemistry,* 158**,** 417-436.

HELCOM (2011) Monitoring of radioactive substances in the Baltic Sea (MORS) (2008-2011). http://www.helcom.fi/projects/on_going/en_GB/mors/, Downloaded 5. April 2011.

HELDAL, H. E. (2001) Radioactivity in Norwegian waters: Distribution in seawater and sediments, and uptake in marine organisms. *Department of Chemistry.* Bergen, University of Bergen.

HELDAL, H. E. (2009) Metode R8: Bestemmelse av Tc-99 i marine miljøprøver ved bruk av rhenium (Re) som tracer og RISØ low-level beta GM multicounter system. *Kvalitetshåndbok for Havforskningsinstituttet, Kjemilaboratoriet.*

HELDAL, H. E., ALVESTAD, P., SVÆREN, I., FØYN, L. & RUDJORD, A. L. (2004) Technetium-99 (Tc-99) i marine næringskjeder i norske havområder. IN SJØTUN, K. (Ed.) *Havets miljø 2004.* Bergen, Havforskningsinstituttet, http://www.imr.no/filarkiv/2004/03/7.10_Tema_Technetium-99_i_marine_naeringskjeder_i_norske_havomrader.pdf/nb-no.

HELDAL, H. E. & SJØTUN, K. (2010) Technetium-99 (99Tc) in annual growth segments of knotted wrack (Ascophyllum nodosum). *Science of the Total Environment,* 408**,** 5575-5582.

HELDAL, H. E., SJØTUN, K. & GWYNN, J. P. (2007a) Technetium-99 in Marine Food Webs in Norwegian Seas - Results from the Norwegian RADNOR project. IN WARWICK, P. (Ed.) *Environmental Radiochemical Analysis III.*

HELDAL, H. E., SVÆREN, I., LIEBIG, P., SJØTUN, K. & WALD, D. (2007b) Technetium-99 (Tc-99) i norske kystområder - Resultater fra "RADNOR". IN DAHL, E., HANSEN, P. K., HAUG, T., KARLSEN, Ø. (Ed.) *Kyst og Havbruk 2007. Fisken og havet særnr. 2, 2007. (In Norwegian).*

HERRMANN, J., KERSHAW, P. J., DU BOIS, P. B. & GUEGUENIAT, P. (1995) The distribution of artificial radionuclides in the English Channel, southern North Sea, Skagerrak and Kattegat, 1990-1993. *Journal of Marine Systems,* 6**,** 427-456.

HOU, X. & ROOS, P. (2008) Critical comparison of radiometric and mass spectrometric methods for the determination of radionuclides in environmental, biological and nuclear waste samples. *Analytica Chimica Acta,* 608**,** 105-139.

HUNT, G. J., SMITH, B. D. & CAMPLIN, W. C. (1998) Recent Changes in Liquid Radioactive Waste Discharges from Sellafield to the Irish Sea: Monitoring of the Environmental Consequences and Radiological Implications *Radiation Protection Dosimetry,* 75**,** 149-153.

IAEA (2004) Sediment distribution coefficients and concentration factors for biota in the marine environment. *Technical Report Series No. 422.* Vienna, IAEA.

ICRP (2007) The 2007 Recommendations of the International Commission on Radiological Protection. ICRP Publication 103. *Ann. ICRP* 37 (2-4).

IFE (2011) The Norwegian Fucus Project *IFE, Institute for Energy Technology,* *http://www.ife.no/departments/health_and_safety/projects/tangprosjektet/view?set_language=en&cl=en*. Kjeller, Downloaded 5. April 2011.

KARCHER, M. J., GERLAND, S., HARMS, I. H., IOSJPE, M., HELDAL, H. E., KERSHAW, P. J. & SICKEL, M. (2004) The dispersion of Tc-99 in the Nordic Seas and the Arctic Ocean: a comparison of model results observations. *Journal of Environmental Radioactivity,* 74**,** 185-198.

KAYE, J. H., MERILL, J. A., KINNISON, R. R., RAPLDS, M. S. & BALLOU, N. E. (1982) Radiochemical Determination of Technetium-99. *Analytical Chemistry,* 54**,** 1158-1163.

KEITH-ROACH, M. J. & ROOS, P. (2004) Redox-dependent behaviour of technetium-99 entering a permanently stratified anoxic fjord (Framvaren fjord, Norway). *Estuarine, Coastal and Shelf Science*, 60**,** 151-161.

KENNA & KURODA (1964) Technetium in nature. *Journal of Inorganic and nuclear chemistry,* 26**,** 493-499.

KERSHAW, P. & BAXTER, A. (1995) The transfer of reprocessing wastes from north-west Europe to the arctic. *Deep-Sea Research Part Ii-Topical Studies in Oceanography,* 42**,** 1413-1448.

KERSHAW, P. J., HELDAL, H. E., MORK, K. A. & RUDJORD, A. L. (2004) Variability in the supply, distribution and transport of the transient tracer Tc-99 in the NE Atlantic. *Journal of Marine Systems,* 44**,** 55-81.

KERSHAW, P. J., MCCUBBIN, D. & LEONARD, K. S. (1999) Continuing contamination of north Atlantic and Arctic waters by Sellafield radionuclides. *Science of the Total Environment,* 238**,** 119-132.

KOFSTAD, P. (1992) *Uorganisk kjemi: en innføring i grunnstoffenes kjemi,* Oslo, TANO.

KOLSTAD, A. K. & LIND, B. (2002) Radioactivity in the Marine Environment 2000 and 2001, Technetium-99 in concentrations in Norwegian coastal waters and biota. *StrålevernRapport 2002:6.* Østerås, Norwegian Radiation Protection Authority.

LEONARD, K. S., MCCUBBIN, D., BROWN, J., BONFIELD, R. & BROOKS, T. (1997) Distribution of technetium-99 in UK coastal waters. *Marine Pollution Bulletin,* 34**,** 628-636.

LEONARD, K. S., MCCUBBIN, D. & LOVETT, M. B. (1995) Physico-chemical characterisation of radionuclides discharged from a nuclear establishment. *Science of the Total Environment,* 175**,** 9-24.

LEONARD, K. S., MCCUBBIN, D., MCDONALD, P., SERVICE, M., BONFIELD, R. & CONNEY, S. (2004) Accumulation of technetium-99 in the Irish Sea? *Science of the Total Environment,* 322**,** 255-270.

LINDAHL, P., ELLMARK, C., GÄFVERT, T., MATTSSON, S., ROOS, P., HOLM, E. & ERLANDSSON, B. (2003) Long-term study of 99Tc in the marine environment on the Swedish west coast. *Journal of Environmental Radioactivity,* 67**,** 145-156.

MARTINIUSSEN, E. (2003) Sellafield. *Bellona rapport Nr.8 - 2003.* Miljøstoftelsen Bellona. Language: Norwegian.

MAS, J. L., GARCIA-LEON, M. & BOLIVAR, J. P. (2004) 99Tc determination in water samples by ICP-MS. *Radiochim. Acta,* 92**,** 39-46.

MASSON, M., VAN WEERS, A. W., GROOTHUIS, R. E. J., DAHLGAARD, H., IBBETT, R. D. & LEONARD, K. S. (1995) Time series for sea water and seaweed of 99Tc and 125Sb originating from releases at La Hague. *Journal of Marine Systems,* 6**,** 397-413.

MATTHÄUS, W. & SCHINKE, H. (1999) The influence of river runoff on deep water conditions of the Baltic Sea. IN BLOMQUIST, E. M., BONSDORFF, E. & ESSINK, K. (Eds.) *Biological, Physical and Geochemical Features of Enclosed and Semi-enclosed Marine Systems.* Kluwer Academic Publishers, Netherlands.

MCCUBBIN, D., LEONARD, K. S., BROWN, J., KERSHAW, P. J., BONFIELD, R. A. & PEAK, T. (2002) Further studies of the distribution of technetium-99 and caesium-137 in UK and European coastal waters. *Continental Shelf Research,* 22**,** 1417-1445.

MCCUBBIN, D., LEONARD, K. S., MCDONALD, P., BONFIELD, R. & BOUST, D. (2006) Distribution of Technetium-99 in sub-tidal sediments of the Irish Sea. *Continental Shelf Research,* 26**,** 458-473.

MYROMS (2011) Regional Ocean Modeling System (ROMS). http://myroms.org/, Downloaded 21. April 2011.

NIES, H., GORONCY, I., HERRMANN, J., MICHEL, R., DARAOUI, A., GORNY, M., JAKOB, D., SACHSE, L., TOSCH, L., NIELSEN, S. P., DAWDALL, M., RUDJORD, A. L., GÄFVERT, T., SYNAL, H.-A., STOCKER, M. & ALFIMOV, V. (2009) Kartierung von Tc-99, I-129 und I-127 im Oberflächenwasser der Nordsee (Mapping of Tc-99, I-129 and I-127 in surface water of the North Sea). *Research project StSch 4481 funded by Bundesamt für Strahlenschutz.* Hamburg and Rostock, Germany, Bundesamt für Seeschifffart und Hydrographie (BSH).

NIES, H., OBRIKAT, D. & HERRMANN, J. (2000) Recent radionuclide concentrations in the North Sea. *Kerntechnik,* 65**,** 195-200.

NRPA (2004) Radioactivity in the Marine Environment 2002. Results from the Norwegian National Monitoring Programme (RAME). *StrålevernRapport 2004:10.* Østerås, Norwegian Radiation Protection Authority.

NRPA (2005) Radioactivity in the Marine Environment 2003. Results from the Norwegian National Monitoring Programme (RAME). *StrålevernRapport 2005:20.* Østerås, Norwegian Radiation Protection Authority.

NRPA (2006) Radioactivity in the Marine Environment 2004. Results from the Norwegian National Monitoring Programme (RAME). *StrålevernRapport 2006:14.* Østerås, Norwegian Radiation Protection Authority.

NRPA (2007) Radioactivity in the Marine Environment 2005. Results from the Norwegian National Monitoring Programme (RAME). *StrålevernRapport 2007:10.* Østerås, Norwegian Radiation Protection Authority.

NRPA (2008) Radioactivity in the Marine Environment 2006. Results from the Norwegian National Monitoring Programme (RAME). *StrålevernRapport 2008:14.* Østerås, Norwegian Radiation Protection Authority.

NRPA (2009) Radioactivity in the Marine Environment 2007. Results from the Norwegian National Monitoring Programme (RAME). *StrålevernRapport 2009:15*. Østerås, Norwegian Radiation Protection Authority.

NRPA (2011) Radioactivity in the Marine Environment 2008 and 2009. Results from the Norwegian National Monitoring Programme (RAME). *StrålevernRapport 2011:4*. Østerås, Norwegian Radiation Protection Authority.

ORRE, S., GAO, Y., DRANGE, H. & NILSEN, J. E. O. (2007) A reassessment of the dispersion properties of Tc-99 in the North Sea and the Norwegian Sea. *Journal of Marine Systems*, 68**,** 24-38.

OSBORNE, P. & HUSTON, R. (2009) Taking the time to listen, learn and act—an example of complex international dialogue. *Journal of Public Affairs*, 9**,** 201-209.

OSPAR (2008) Liquid discharges from nuclear installations in 2006, including exceptional discharges from decommissioning and management of legacy radioactive wastes. *OSPAR Commission, Radioactive Substances Series*, http://www.ospar.org/documents/dbase/publications/p00382_Liquid%20Discharges%20data%20report%202006.pdf.

OSPAR (2009a) Liquid discharges from nuclear installations in 2007. *OSPAR Commission, Radioactive Substances Series*, http://www.ospar.org/documents/dbase/publications/p00456_Liquid%20Discharges%20data%20report%202007.pdf.

OSPAR (2009b) Towards the Radioactive Substances Strategy objectives, Third Periodic Evaluation. *OSPAR Commission, Radioactive Substances Series*, http://www.ospar.org/documents/dbase/publications/p00455_3PE.pdf.

OSPAR (2010a) Liquid discharges from nuclear installations in 2008. *OSPAR Commission, Radioactive Substances Series*, http://www.ospar.org/documents/dbase/publications/p00515_Liquid%20Discharges%20data%20report%202008.pdf.

OSPAR (2010b) Quality Status Report 2010, Chapter 6 Radioactive Substances. OSPAR Commission, http://qsr2010.ospar.org/en/media/chapter_pdf/QSR_Ch06_EN.pdf.

OSPAR (2011) About Ospar. http://www.ospar.org/, Downloaded 22. April 2011.

OTTO, L., ZIMMERMAN, J., FURNES, G. K., MORK, M., SÆTRE, R. & BECKER, G. (1990) Review of the physical oseanography of the North Sea. *Netherlands Journal of Sea Research*, 26**,** 161-238.

PERRIER, C. & SEGRÉ, E. (1937) Radioactive Isotopes of Element 43. *Nature*, 140**,** 193-194.

PERRIER, C. & SEGRÉ, E. (1947) Technetium : The Element of Atomic Number 43. *Nature*, 159**,** 24-24.

REGJERINGEN.NO (2002) Report No.12 to the Storting (2001-2002), Protecting the Riches of the Seas. Chapter 3.4: Radioactive pollution. *Royal Ministry of the Environment*. http://www.regjeringen.no/en/dep/md/documents-and-publications/government-propositions-and-reports-/Reports-to-the-Storting-white-papers-2/20012002/Report-No-12-2001-2002-to-the-Storting/3/4.html?id=452069

RIFE-1 (1996) Radioactivty in Food and the Environment, 1995. *Ministry of Agriculture, Fisheries and Food*.

RIFE-2 (1997) Radioactivity in Food and the Environment, 1996. *Ministry of Agriculture, Fisheries and Food, Scottish Environment Protection Agency*.

RIFE-3 (1998) Radioactivty in Food and the Environment, 1997. *Ministry of Agriculture, Fisheries and Food, Scottish Environment Protection Agency*.

RIFE-4 (1999) Radioactivty in Food and the Environment, 1998. *Ministry of Agriculture, Fisheries and Food, Scottish Environment Protection Agency*.

RIFE-5 (2000) Radioactivty in Food and the Environment, 1999. *Food Standards Agency, Scottish Environment Protection Agency*.

RIFE-6 (2001) Radioactivty in Food and the Environment, 2000. *Food Standards Agency, Scottish Environment Protection Agency*.

RIFE-7 (2002) Radioactivty in Food and the Environment, 2001. *Food Standards Agency, Scottish Environment Protection Agency*.

RIFE-8 (2003) Radioactivty in Food and the Environment, 2002. *Environment Agency, Environment and Heritage Service, Food Standards Agency, Scottish Environment Protection Agency*.

RIFE-9 (2004) Radioactivity in Food and the Environment, 2003. *Environment Agency, Environment and Heritage Service, Food Standards Agency, Scottish Environment Protection Agency*.

RIFE-10 (2005) Radioactivty in Food and the Environment, 2004. *Environment Agency, Environment and Heritage Service, Food Standards Agency, Scottish Environment Protection Agency*.

RIFE-11 (2006) Radioactivty in Food and the Environment, 2005. *Environment Agency, Environment and Heritage Service, Food Standards Agency, Scottish Environment Protection Agency*.

RIFE-12 (2007) Radioactivty in Food and the Environment, 2006. *Environment Agency, Environment and Heritage Service, Food Standards Agency, Scottish Environment Protection Agency*.

RIFE-13 (2008) Radioactivty in Food and the Environment, 2007. *Environment Agency, Food Standards Agency, Northern Ireland Environment Agency, Scottish Environment Protection Agency*.

RIFE-14 (2009) Radioactivty in Food and the Environment, 2008. *Environment Agency, Food Standards Agency, Northern Ireland Environment Agency, Scottish Environment Protection Agency*.

RIFE-15 (2010) Radioactivty in Food and the Environment, 2009. *Environment Agency, Food Standards Agency, Northern Ireland Environment Agency, Scottish Environment Protection Agency*.

RISØ (2009) User Manual Low-level beta GM multicounter System Model Risø GM-25-5A.

RUDJORD, A. L., FØYN, L., BRUNGOT, A. L., KOLSTAD, A. K., HELDAL, H. E., BROWN, J., IOSJPE, M. & CHRISTENSEN, G. (2001) Radioactivity in the Marine Environment (RAME) 1999. *StrålevernRapport 2001:9.* Østerås, Norwegian Radiation Protection Authority.

SAFETYATSEA (2011) Currents in the North Sea. http://www.safetyatsea.se/index.php?art=2041&group=400, Downloaded 5. April 2011.

SALBU, B. & HOLM, E. (2005) RADIOCHEMICAL METHODS: Technetium. *Encyclopedia of Analytical Science.*

SARMIENTO, J. L. & GRUBER, N. (2006) *Ocean biogeochemical dynamics,* Princeton, N.J., Princeton University Press.

SELLAFIELD.LTD (2011) http://www.sellafieldsites.co.uk/. Downloaded 21. April 2011.

SJØTUN, K., HELDAL, H. E. & BRAKSTAD, D. S. (Submitted for publication) Differential concentration of Technetium-99 (^{99}Tc) in common intertidal molluscs with different food habits. *Marine Pollution Bulletin*.

SMITH, V., FEGAN, M., POLLARD, D., LONG, S., HAYDEN, E. & RYAN, T. P. (2001) Technetium-99 in the Irish marine environment. *Journal of Environmental Radioactivity,* 56**,** 269-284.

SMITH, V., FEGAN, M., WONG, J. & LONG, S. (2009) The dose to Irish seafood consumers from Technetium-99. *Radioprotection*, 44**,** 425-429.

STEEN, H. (2008) Grisetanghøsting. *Veileder kystsone.no*, *http://www.kystsone.no/news.cfm?newsitemid=753*. Downloaded 5. April 2011.

STEEN, H. (2009) Tang og tare. *IMR, Insitute of Marine Research*, *http://www.imr.no/temasider/alger/tang_og_tare/46389/nb-no*. Downloaded 5. April 2011.

STRÅLEVERNINFO (2004) StrålevernInfo 2004:08. *StrålevernInfo.* Østerås, Norwegian Radiation Protection Authority. Language: Norwegian.

SÆTRE, R. (2007) *The Norwegian coastal current: oceanography and climate*, Trondheim, Institute of Marine Research.

THØRRING, H., YTRE-EIDE, M. A. & LILAND, A. (2010) Consequences in Norway after a hypothetical accident at Sellafield - Predicted impacts on the environment. *StrålevernRapport 2010:13.* Østerås, Norwegian Radiation Protection Authority.

UMB (2009) Lecture notes KJM351 autumn 2009, Brit Salbu. *Norwegian University of Life Sciences, Ås, Norway*.

VINTRÓ, L. L. (2009) Marine Radioecology: a brief introduction. *Lecture in European master in Radioecology 2009/2010 (KJM351).* Norwegian University of Life Sciences (UMB), Ås, Norway, UCD School of Physics, University College Dublin.

VINTRÓ, L. L., SMITH, K. J., LUCEY, J. A. & MITCHELL, P. I. (2001) The environmental impact on the Sellafield discharges. *http://homepage.eircom.net/~radphys/scope.pdf*, Expert Group Meeting, Scientific Committee on Problems of the Environment of the International Council of Scientific Unions, Brussels, 4-6 December 2000.

YIOU, F., RAISBECK, G. M., CHRISTENSEN, G. C. & HOLM, E. (2002) I-129/I-127, I-129/Cs-137 and I-129/Tc-99 in the Norwegian coastal current from 1980 to 1998. *Journal of Environmental Radioactivity*, 60**,** 61-71.

YTRE-EIDE, M. A., STANDRING, W. J. F., AMUNDSEN, I., SICKEL, M., LILAND, A., SALTBONES, J., BARTNICKI, J., HAAKENSTAD, H. & SALBU, B. (2009) Consequences in Norway of a hypothetical accident at Sellafield: Potential release – transport and fallout. *StrålevernRapport 2009:7.* Østerås, Norwegian Radiation Protection Authority.

AARKROG, A., BOELSKIFTE, S., DAHLGAARD, H., DUNIEC, S., HALLSTADIUS, L., HOLM, E. & SMITH, J. (1987) Technetium-99 as a long distance tracer in Arctic waters. *Estuarine, Coastal and Shelf Science*, 24**,** 637-647.

AARKROG, A., CARLSSON, L., CHEN, Q., DAHLGAARD, H., HOLM, E., HUYNH-NGOC, L., JENSEN, L. H., NIELSEN, S. P. & NIES, H. (1988) Origin of technetium-99 and its use as marine tracer. *Nature*, 335**,** 338-340.

AARKROG, A., DAHLGAARD, H., HALLSTADIUS, L., HOLM, E., MATTSSON, S. & RIOSECO, J. (1986) Time trend of ^{99}Tc in seaweed from Greenland waters. IN DESMET, G. & MYTTENAERE, C. (Eds.) *Technetium in the Environment.* New York, Elsevier.

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Appendices

APPENDIX 1: The Nuclear Fuel Cycle

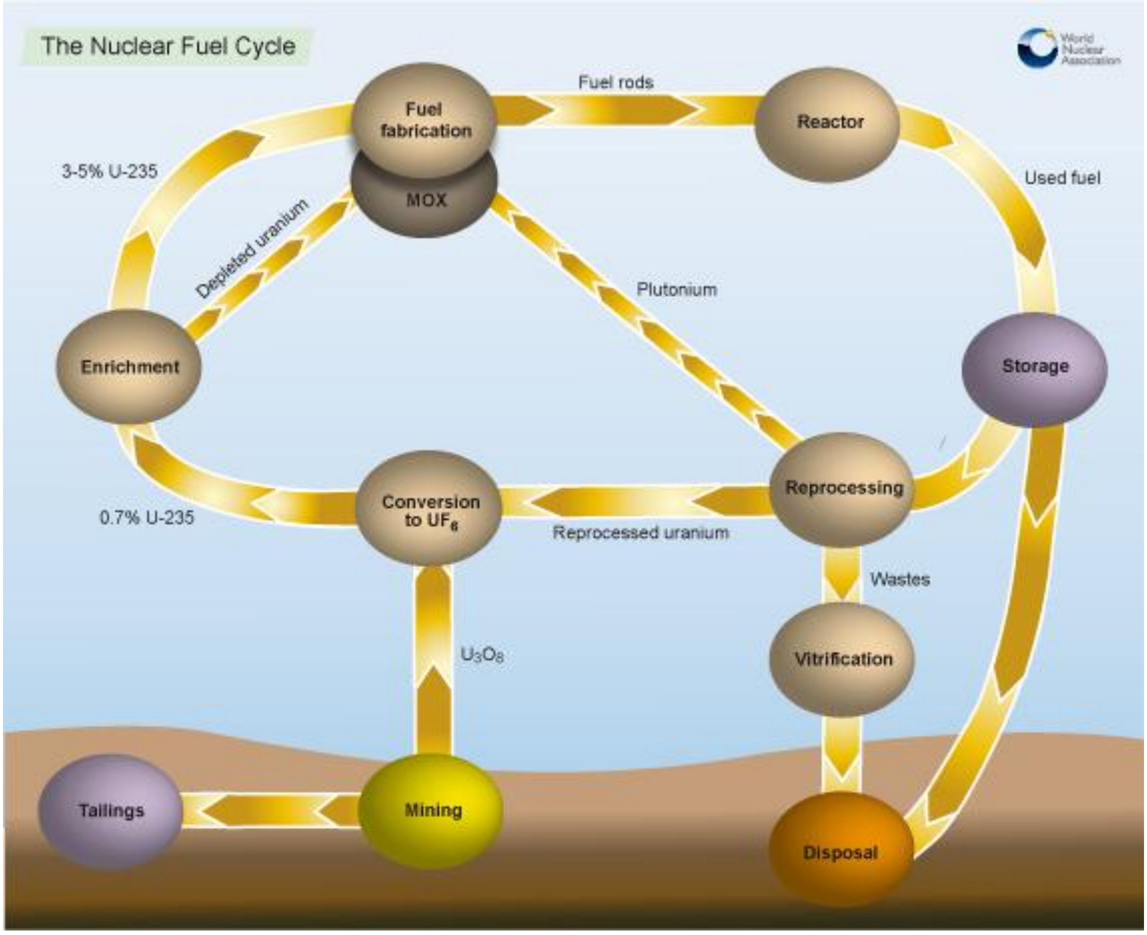

Figure A1.9: The Nuclear Fuel Cycle. Figure from http://www.world-nuclear.org/info/inf03.html (date: 10.12.2010)

- Extraction of uranium
    - Extract uranium from ores as ”yellow cake”, approximately 70 – 90 % U_3O_8
- Naturally uranium consists of:
    - 99,275 % ^{238}U, $t_{1/2} = 4.5 \cdot 10^9$ years
    - 0,720 % ^{235}U, $t_{1/2} = 7 \cdot 10^8$ years
    - 0,005 % ^{234}U, $t_{1/2} = 2.5 \cdot 10^5$ years
- Enrichment of uranium:
    - Removal of all other elements by chemical separation
    - Isotopes are separated physically
        - by gas diffusion:
            - Uranium oxide → UF_6 gas at high temperature

        - The gas is pushed through thin”filters”, and since ^{235}U has lower mass than ^{238}U, ^{235}U passes the filter fastest.
    - By centrifugation: smaller masses separate from fractions with higher masses.
  - Enriched uranium for civil reactors contain 3% ^{235}U
- Fuel fabrication: UO_2 pellets, fissionable fuel material
- Fission of uranium in a reactor:

  $^{235}U + n \rightarrow [^{236}U] \rightarrow$ fission product + 2.5 n + Q (energy)
- Reprocessing: The spent fuel are taken out of the reactor after approximately 3 years in the reactor
  - Stored under water: short lived radionuclides decay
  - Uranium and plutonium (Pu) are extracted using different processes: acidic and organic solvents dissolves fission products, but does not dissolve U and Pu
  - U and Pu are then extracted an separated from each other using chemicals that precipitates Pu while U remains in solution
- Reprocessing plants: Most reprocessing plants began as weapon production sites, producing U and Pu for nuclear weapons. Today the focus has changed from military to civil as the plants are now using their knowledge in reprocessing of spent fuel from nuclear power plants.
  - European plants
    - Sellafield, UK
    - La Hague, France
    - (Dounray, UK)
  - Russian plants
    - Mayak PA
    - Krasnoyarsk-26
    - Tomsk, SCC

- Radioactive waste classification: Wastes from the nuclear fuel cycle are categorized as high, medium- or low-level waste depending on the amount of radiation that they emit.
  - High level waste:
    - Used fuel:
      - Fission products (“short” half-life)
      - Actinides (neutron activated uranium) and ^{99}Tc (long half-life)

        - Neutron activated reactor materials
    - intermediate-level waste
        - waste produced during reactor operation and by reprocessing
    - Low level waste
        - Waste from secondary circuit

References

Norwegian University of Life Sciences (2009) *KJM351 lecture notes*, Ås, Norway

World Nuclear Association (August 2010) *The Nuclear Fuel Cycle*. http://www.world-nuclear.org/info/inf03.html (Date: 10.12.2010)

APPENDIX 2: Temperature, salinity and density of seawater

Salinity

The Practical Salinity Scale defines salinity in terms of the conductivity ratio of a sample to that of a solution of 32.4356 g of KCl at 15°C and a pressure of 1 standard atmosphere in a 1 kg solution (http://www.ices.dk/ocean/procedures/standard_seawater.htm). A sample of seawater at 15°C with conductivity equal to this KCl solution has a salinity of exactly 35. Because salinity is defined as a ratio, it is not given with units. PSU (practical salinity unit) or per mille is sometimes used as a unit, but salinity should not have a unit.

Density of seawater

Density (ρ) (kg m^{-3}) is a function of temperature (T), salinity (S) and pressure (p): $\rho = f(T, S, p)$. In oceanography, density is given as the potential density $\sigma = (\rho - 1000)$. Surfaces of constant potential density are referred to as isopycnal surfaces or isopycnals. The relationship between temperature, salinity and density is shown in figure A2.1. The density of seawater with salinity 35 at 15 °C is about 1025.5 kg m^{-3}, or σ (sigma) = 25.5. The equation of state of seawater is quite complex, but a simple rule of thumb is that the density increases by roughly 1 (sigma) when the temperature decreases by 5 °C, the salinity increases by 1 psu or the pressure increases by 200 dbar (about 200 m depth). (http://fermi.jhuapl.edu/denscalc.html, (Sarmiento and Gruber, 2006). (The saltier the water is, the higher its density. When water warms, it expands and becomes less dense. Contrary, the colder the water, the denser it becomes.)

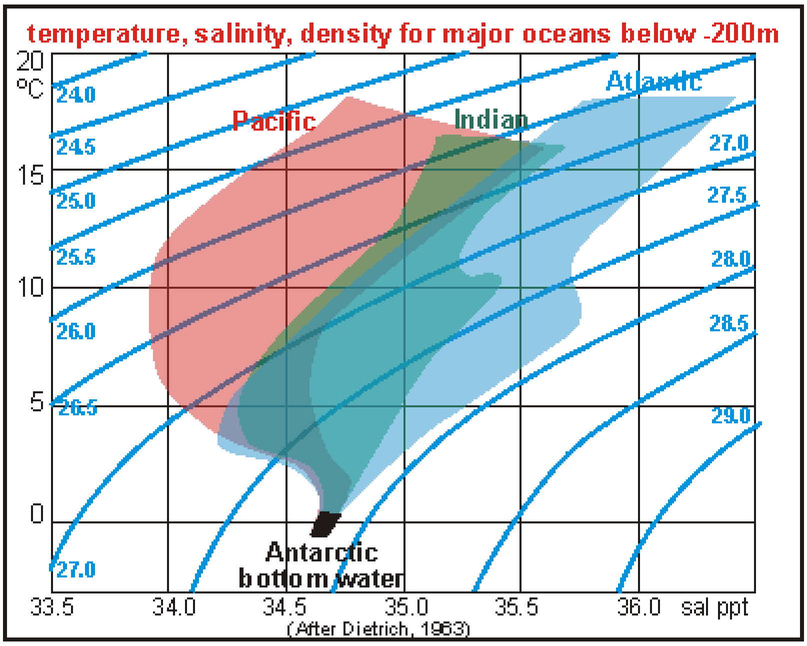

Figure A2.1: The relationship between temperature, salinity and density is shown by the isopycnal (lines of constant density) curves in this diagram (http://www.seafriends.org.nz/oceano/seawater.htm#Density.)

References

http://www.ices.dk/ocean/procedures/standard_seawater.htm (date: 22.04.2011)
http://fermi.jhuapl.edu/denscalc.html (date: 22.04.2011)
http://www.seafriends.org.nz/oceano/seawater.htm#Density (date: 22.04.2011)

SARMIENTO, J. L. & GRUBER, N. (2006) *Ocean biogeochemical dynamics,* Princeton, N.J., Princeton University Press.

APPENDIX 3: Reagents

Rhenium solution: A 4 mg Re/ml – solution was prepared by dissolving 0.6215 g potassium perrhenate, $KReO_4$ (99.99 %, Sigma-Aldrich Norway AS) in distilled water and diluted to 100 ml. (The potassium perrhenate was dried at 105 ± 5 °C over night and cooled in a desiccator).

Anion exchange resin (for pre-concentration): Anion exchange columns for pre-concentration of technetium and rhenium from 100 L seawater samples were made by packing 55 ml anion exchange resin (Amberlite IRA-400 chloride form, Sigma-Aldrich Norway AS) into 50 ml polypropene syringes, containing a bottom and top fiber pad to support the resin.

Anion exchange resin (for the anion exchange separation step): The columns were made up by filling approximate 1.5 ml BioRad AG 1x8 (100-200 chloride) (Bio-Rad Laboratories) into 14 cm long Pasteur pipettes containing a small plug of glass wool to support the resin. Each anion exchange column was attached to a funnel containing 240 mm Whatman No. 542 filter paper, by means of a piece of plastic tubing.

Hydrogenperoxide (H_2O_2) 30 % vol (VWR International AS)

Hydrochloric acid (HCl): A 6 M HCl solution is prepared by diluting 530 ml concentrated hydrochloric acid (37%) (VWR International AS) in distilled water to 1 L

Sodium hydroxide (NaOH): A 6 M NaOH solution is prepared by dissolving 240 g NaOH pellets (VWR International AS) in distilled water and diluting to 1 L. A 2 M NaOH solution is prepared by dissolving 80 g NaOH pellets in distilled water and diluting to 1 L.

Ammonium hydroxide (NH_4OH): ~ 28 % NH_3 in H_2O (Sigma-Aldrich Norway AS), used as supplied.

Fe^{3+} solution: prepared by dissolving 96.2 g of iron(III) chloride-6-hydrate, $FeCl_3{\cdot}6H_2O$ (VWR International AS) in 6 M HCl and dilute to 1 L. This gives a solution of 20 mg Fe^{3+}/ml. To be contained in a brown glass bottle.

Sodium perchlorate solution (0.3 M NaOH / 0.15 $HClO_4$): prepared by dissolving 12 g NaOH pellets (VWR International AS) in distilled water, adding 25 ml perchloric acid, $HClO_4$ (Sigma-Aldrich Norway AS) and diluting to 1 L.

Thioacetamide (CH_3CSNH_2) (Sigma-Aldrich Norway AS): used as the solid supplied.

Tetraphenyl arsonium chloride solution: prepared by dissolving 2.75 g tetraphenyl arsonium chloride ($(C_6H_5)_4AsCl{\cdot}H_2O$) (Sigma-Aldrich Norway AS) in distilled water and dilute to 500 ml.

APPENDIX 4: Calculation of results

Table A4.1: Calculation of ^{99}Tc activity concentrations and uncertainties using Excel

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U
1	Prøve ID	Målt på	Filnavn	Jnr.	Volum sjøvatn	Vekt	Vekt filter +	Vekt	Mengde	Utbytte	Effektivitet	cps	cps	ncps	Telletid (s)	100	100	1000	***Bq***	***mBq/L***	*± (%)*
2		detektor nr.			L (L)	filter (g)	bunnfall (g)	bunnfall (g)	tils. Re	%	%	prøve	bakgrunn	prøve	prøve	utbytte (%)	effektivitet	volum (L)			
3	*FORMULA*							*GX-FX*		*(HX*100)/0,0272*				*LX-MX*		*100/JX*	*100/KX*	*1000/EX*	*NX*PX*QX*	*NX*PX*QX*RX*	***SQRT((100*(SQRT((LX/OX)+(MX/172800)))/(LX-MX))^2+25***
4																					
5	JH 050710 OF st 498 (T10)	1	sa100816	1241	102,1	0,0229	0,0433	0,0204	8 mg	75	21,83	0,0092	0,0024	0,0068	172800	1,3333	4,58	9,79		***0,41***	***6,3***
6	JH 060710 OF st 503 (T9)	2	sa100816	1241	102,2	0,0230	0,0428	0,0198	8 mg	72,79	22,46	0,0089	0,0022	0,0067	172800	1,3737	4,45	9,78		***0,40***	***6,3***
7	JH 070710 OF st 505	3	sa100816	1241	102,9	0,0227	0,0426	0,0199	8 mg	73,16	22,28	0,0088	0,0023	0,0065	172800	1,3668	4,49	9,71		***0,39***	***6,3***
8	JH 070710 OF st 506	4	sa100816	1241	103,1	0,0230	0,0398	0,0168	8 mg	61,76	23,44	0,0079	0,0023	0,0056	172800	1,6190	4,27	9,70		***0,38***	***6,6***
9	JH 080710 OF st 507	5	sa100816	1241	102,4	0,0227	0,0450	0,0223	8 mg	81,99	21,48	0,0092	0,0024	0,0068	172800	1,2197	4,66	9,77		***0,38***	***6,3***
10																					
11	JH 080710 OF st 508	1	sa100818	1241	104,2	0,0229	0,0441	0,0212	8 mg	77,94	21,55	0,0080	0,0024	0,0056	172800	1,2830	4,64	9,60		***0,32***	***6,7***
12	JH 080710 OF st X	2	sa100818	1241	103,6	0,0231	0,0442	0,0211	8 mg	77,57	21,98	0,0078	0,0022	0,0056	172800	1,2891	4,55	9,66		***0,32***	***6,6***
13	JH 080710 OF st 509	3	sa100818	1241	98,5	0,0228	0,0441	0,0213	8 mg	78,31	21,79	0,0086	0,0023	0,0063	172800	1,2770	4,59	10,16		***0,38***	***6,4***
14	BLK 160810	4	sa100818			0,0228	0,0486	0,0258	8 mg	94,85	20,32	0,0025	0,0023	0,0002	172800	1,0543	4,92		***0,001***		***81,19***
15	KK 160810	5	sa100818			0,0229	0,0466	0,0237	8 mg	87,13	21,04	0,2367	0,0024	0,2343	172800	1,1477	4,75		***1,278***		***5,03***
16																					
17	JH 100710 OF st 516	1	sa100824	1241	98,1	0,0227	0,0429	0,0202	8 mg	74,26	21,90	0,0093	0,0024	0,0069	172800	1,3465	4,57	10,19		***0,43***	***6,3***
18	JH 130710 OF st 535 (T26)	2	sa100824	1241	102,7	0,0229	0,0433	0,0204	8 mg	75	22,23	0,0069	0,0022	0,0047	172800	1,3333	4,50	9,73		***0,27***	***7,0***
19	JH 150710 OF st 545	3	sa100824	1241	102,3	0,0225	0,0435	0,0210	8 mg	77,21	21,89	0,0080	0,0023	0,0057	172800	1,2952	4,57	9,78		***0,33***	***6,6***
20	JH 170710 OF st 549	4	sa100824	1241	103,0	0,0226	0,0424	0,0198	8 mg	72,79	22,24	0,0075	0,0023	0,0052	172800	1,3737	4,50	9,71		***0,31***	***6,8***
21	JH 180710 OF st 555 (T11)	5	sa100824	1241	102,8	0,0226	0,0429	0,0203	8 mg	74,63	22,16	0,0083	0,0024	0,0059	172800	1,3399	4,51	9,73		***0,35***	***6,5***
22																					
23	JH 190710 OF st 576	1	sa100827	1241	100,4	0,0226	0,0385	0,0159	8 mg	58,46	23,59	0,0043	0,0024	0,0019	172800	1,7107	4,24	9,96		***0,14***	***11,6***
24	JH 190710 OF st 586	2	sa100827	1241	101,2	0,0225	0,0438	0,0213	8 mg	78,31	21,91	0,0156	0,0022	0,0134	172800	1,2770	4,56	9,88		***0,77***	***5,5***
25	JH 260710 OF st 596	3	sa100827	1242	101,2	0,0227	0,0448	0,0221	8 mg	81,25	21,52	0,0044	0,0023	0,0021	172800	1,2308	4,65	9,88		***0,12***	***10,7***

APPENDIX 4

Table A4.1 (continued): Calculation of ^{99}Tc activity concentrations and uncertainties using Excel

26	BLK 240810	4	sa100827			0,0226	0,0448	0,0222	8 mg	81,62	21,41	0,0026	0,0023	0,0003	172800	1,2252	4,67		***0,002***		***60,02***
27	KK 240810	5	sa100827			0,0229	0,0484	0,0255	8 mg	93,75	20,50	0,2234	0,0024	0,2210	172800	1,0667	4,88		***1,150***		***5,03***
28																					
29	*JH 050309 st 68*	*1*	*sa101121*		*105,8*	*0,0226*	*0,0467*	*0,0241*	*8 mg*	*88,60*	*20,64*	*0,0073*	*0,0025*	*0,0048*	*172800*	*1,1286*	*4,84*	*9,46*		***0,25***	***7,0***
30	*JH 050309 st 78*	*2*	*sa101121*		*106,1*	*0,0225*	*0,0446*	*0,0221*	*8 mg*	*81,25*	*21,63*	*0,0041*	*0,0023*	*0,0019*	*172800*	*1,2308*	*4,62*	*9,42*		***0,10***	***11,4***
31	*JH 280909 OF st 624*	*3*	*sa101121*		*102,6*	*0,0229*	*0,0447*	*0,0218*	*8 mg*	*80,15*	*21,62*	*0,0060*	*0,0023*	*0,0037*	*172800*	*1,2477*	*4,63*	*9,75*		***0,21***	***7,7***
32	*JH 290909 OF st 630*	*4*	*sa101121*		*98,4*	*0,0229*	*0,0447*	*0,0218*	*8 mg*	*80,15*	*21,55*	*0,0044*	*0,0023*	*0,0022*	*172800*	*1,2477*	*4,64*	*10,16*		***0,13***	***10,4***
33	JH 290710 OF st 615 (T27)	5	sa101121	1242	101,1	0,0228	0,0439	0,0211	8 mg	77,57	21,88	0,0058	0,0024	0,0033	172800	1,2891	4,57	9,89		***0,20***	***8,2***
34																					
35	JH 270710 OF st 608	1	sa101130	1242	105,3	0,0227	0,0450	0,0223	8 mg	81,99	21,19	0,0075	0,0025	0,0051	172800	1,2197	4,72	9,50		***0,28***	***6,9***
36	JH 310710 OF st 624	2	sa101130	1242	100,0	0,0228	0,0448	0,0220	8 mg	80,88	21,67	0,0049	0,0023	0,0026	172800	1,2364	4,61	10,00		***0,15***	***9,2***
37	JH 010810 OF st 627	3	sa101130	1243	98,3	0,0228	0,0460	0,0232	8 mg	85,29	21,17	0,0081	0,0023	0,0058	172800	1,1724	4,72	10,17		***0,33***	***6,5***
38	BLK 130910	4	sa101130			0,0229	0,0480	0,0251	8 mg	92,28	20,52	0,0023	0,0023	0,0001	172800	1,0837	4,87		***0,00033***		***260***
39	KK 130910	5	sa101130			0,0228	0,0473	0,0245	8 mg	90,07	20,80	0,2152	0,0024	0,2128	172800	1,1102	4,81		***1,136***		***5,03***

APPENDIX 5: ^{99}Tc results 1998-2010

Table A5.1: ^{99}Tc activity concentrations in 1998

Area	Ship	Station	Sampling date	Latitude		Longitude		Depth (m)	Sampling depth (m)	Salinity	Temperature (ºC)	^{99}Tc (Bq m^{-3})	Error ± (%)	Error ± (Bq m^{-3})	Reference
Norwegian Sea	M. Sars	629	03.07.98	72,80	N	13,85	E	1133	5	34,776	8,444	0,28	10,5	0,03	1
Norwegian Sea	M. Sars	630	03.07.98	73,57	N	16,12	E	452	5	35,005	7,266	0,25	7,3	0,02	1
Norwegian Sea	M. Sars	631	04.07.98	74,35	N	18,42	E	73	5	34,616	1,406	0,08	15,8	0,01	1
Norwegian Sea	M. Sars	634	04.07.98	74,98	N	18,30	E	94	5	34,077	3,172	0,13	10,4	0,01	1
Norwegian Sea	M. Sars	644	05.07.98	76,33	N	16,18	E	77	5	32,647	-0,366	bd	-		1
Norwegian Sea	M. Sars	645	06.07.98	76,92	N	12,50	E	746	5	34,371	5,233	0,08	19,7	0,02	1
Norwegian Sea	M. Sars	647	06.07.98	76,92	N	13,50	E	101	5	32,348	2,746	0,16	9,8	0,02	1
Norwegian Sea	M. Sars	650	06.07.98	76,97	N	15,50	E	150	5	32,626	1,567	0,06	24,9	0,01	1
Norwegian Sea	M. Sars	672	09.07.98	71,50	N	19,80	E	236	5	34,661	9,150	0,42	5,4	0,02	1
Norwegian Sea	M. Sars	675	09.07.98	71,00	N	19,90	E	190	5	34,462	9,897	0,65	5,0	0,03	1
Norwegian Sea/NwCC north of Stad	M. Sars	678	09.07.98	70,50	N	20,00	E	126	5	33,863	10,979	0,86	4,5	0,04	1
Norwegian Sea/NwCC north of Stad	M. Sars	678	09.07.98	70,50	N	20,00	E	126	30	34,554	7,161	0,80	4,5	0,04	1

highlighted=sample from the water column

bd=below detection limit
1 Kershaw et al., 2004.

KERSHAW, P. J., HELDAL, H. E., MORK, K. A. & RUDJORD, A. L. (2004) Variability in the supply, distribution and transport of the transient tracer Tc-99 in the NE Atlantic. Journal of Marine Systems, 44, 55-81.

APPENDIX 5

Table A5.2: ^{99}Tc activity concentrations in 1999

Area	Ship	Station	Sampling date	Latitude		Longitude		Depth (m)	Sampling depth (m)	Salinity	Temperature (ºC)	^{99}Tc (Bq m^{-3})	Error ± (%)	Error ± (Bq m^{-3})	Reference
Norwegian Sea / NwCC north of Stad	J. Hjort	462	18.06.99	68,43	N	14,02	E	110	5	33,616	8,214	1,61	4,2	0,07	1
Norwegian Sea / NwCC north of Stad	J. Hjort	470	18.06.99	68,85	N	12,80	E	660	5	34,912	9,245	0,52	4,9	0,03	1
Greenland Sea / EGC	J. Hjort	491	24.06.99	74,50	N	-14,62	W	267	5	32,823	-0,041	0,13	10,9	0,01	1
Greenland Sea / EGC	J. Hjort	491	24.06.99	74,50	N	-14,62	W	267	30	33,925	0,077	0,09	18,3	0,02	1
Norwegian Sea / Greenland Sea	J. Hjort	501	26.06.99	74,50	N	3,00	E	3320	5	34,738	2,164	0,09	20,6	0,02	1
Norwegian Sea / Greenland Sea	J. Hjort	505	27.06.99	74,50	N	11,00	E	2390	5	35,100	6,020	0,21	8,5	0,02	1
Norwegian Sea / Greenland Sea	J. Hjort	507	28.06.99	74,50	N	14,00	E	2106	5	35,103	6,328	0,26	6,5	0,02	1
Norwegian Sea / Greenland Sea	J. Hjort	512	28.06.99	74,50	N	16,67	E	193	5	35,090	6,927	0,25	6,4	0,02	1
Norwegian Sea / NwCC north of Stad	J. Hjort	516	01.07.99	70,50	N	20,00	E	146	5	33,812	9,212	1,49	4,1	0,06	1
Norwegian Sea / NwCC north of Stad	J. Hjort	522	01.07.99	71,50	N	19,80	E	236	5	34,663	9,431	0,93	4,4	0,04	1
Norwegian Sea / Greenland Sea	J. Hjort	530	02.07.99	73,50	N	19,33	E	480	5	35,054	6,680	0,26	7,3	0,02	1
Norwegian Sea / Greenland Sea	J. Hjort	535	02.07.99	74,25	N	19,17	E	58	5	34,920	3,605	0,22	7,5	0,02	1
Norwegian Sea / Greenland Sea	J. Hjort	539	03.07.99	76,58	N	20,00	E	205	5	33,536	1,888	0,11	13,2	0,01	1

highlighted=sample from the water column

EGC= East Greenland Current
1 Kershaw et al., 2004

APPENDIX 5

Table A5.3: ^{99}Tc activity concentrations in 2000

Area	Ship	Station	Sampling date	Latitude		Longitude		Depth (m)	Sampling depth (m)	Salinity	Temperature (ºC)	^{99}Tc (Bq m^{-3})	Error ± (%)	Error ± (Bq m^{-3})	Reference
Norwegian Sea / Greenland Sea	J. Hjort	373	28.05.00	69,48	N	10,94	E	2954	5	35,132	7,329	0,27	5,12	0,01	1
Norwegian Sea / Greenland Sea	J. Hjort	388	31.05.00	74,08	N	-3,67	W	3494	5	34,835	-0,067	0,05	11,1	0,01	1
Norwegian Sea / Greenland Sea	J. Hjort	389	01.06.00	74,50	N	-11,72	W	2955	5	34,327	-0,653	0,10	7,15	0,01	1
Norwegian Sea / Greenland Sea	J. Hjort	394	02.06.00	74,50	N	-3,00	W	3601	5	34,842	0,487	0,05	12,4	0,01	1
Norwegian Sea / Greenland Sea	J. Hjort	396	03.06.00	74,50	N	0,00	E	3740	5	34,830	0,411	0,05	16,2	0,01	1
Norwegian Sea / Greenland Sea	J. Hjort	398	03.06.00	74,50	N	3,00	E	3354	5	34,823	1,360	0,08	10,0	0,01	1
Norwegian Sea / Greenland Sea	J. Hjort	402	04.06.00	74,50	N	11,00	E	2396	5	35,087	5,558	0,30	4,65	0,01	1
Norwegian Sea / Greenland Sea	J. Hjort	404	04.06.00	74,50	N	13,99	E	2112	5	35,074	6,012	0,39	4,50	0,02	1
Norwegian Sea / Greenland Sea	J. Hjort	408	05.06.00	74,50	N	16,50	E	252	5	35,072	5,952	0,38	4,44	0,02	1
Norwegian Sea / Greenland Sea	J. Hjort	412	05.06.00	74,50	N	18,50	E	64	5	34,628	0,392	0,22	5,40	0,01	1
Norwegian Sea / Greenland Sea	J. Hjort	425	07.06.00	75,82	N	17,58	E	247	5	34,023	0,848	0,20	5,61	0,01	1
Norwegian Sea / Greenland Sea	J. Hjort	427	07.06.00	75,71	N	15,59	E	382	5	33,690	0,538	0,22	5,02	0,01	1
Norwegian Sea / Greenland Sea	J. Hjort	431	08.06.00	75,50	N	12,00	E	1986	5	35,091	5,277	0,27	4,75	0,01	1
Norwegian Sea / Greenland Sea	J. Hjort	432	08.06.00	76,33	N	10,41	E	2168	5	35,050	4,466	0,25	4,86	0,01	1
Norwegian Sea / Greenland Sea	J. Hjort	435	08.06.00	76,34	N	16,00	E	102	5	33,858	-0,021	0,20	5,67	0,01	1
Norwegian Sea / Greenland Sea	J. Hjort	436	09.06.00	77,33	N	13,75	E	73	5	33,567	0,128	0,21	5,08	0,01	1
Norwegian Sea / Greenland Sea	J. Hjort	439	09.06.00	77,33	N	10,92	E	1076	5	34,802	4,000	0,30	4,63	0,01	1
Norwegian Sea / Greenland Sea	J. Hjort	442	10.06.00	74,25	N	19,17	E	60	5	34,697	0,224	0,19	5,27	0,01	1
Norwegian Sea / Greenland Sea	J. Hjort	451	11.06.00	72,50	N	19,57	E	389	5	35,087	6,275	0,35	4,61	0,02	1
NwCC north of Stad	J. Hjort	461	12.06.00	70,50	N	20,00	E	126	5	34,464	7,101	1,19	4,09	0,05	1
NwCC north of Stad	M. Sars	653	14.06.00	71,00	N	26,50	E	279	5	33,561	6,347	0,72	4,47	0,03	1
NwCC north of Stad	M. Sars	654	14.06.00	71,17	N	26,50	E	165	5	34,553	6,232	0,63	4,49	0,03	1
NwCC north of Stad	M. Sars	655	14.06.00	71,33	N	25,00	E	301	5	34,543	6,421	0,72	4,43	0,03	1
NwCC north of Stad	M. Sars	656	14.06.00	71,17	N	25,00	E	155	5	33,759	5,774	0,69	4,45	0,03	1
NwCC north of Stad	M. Sars	658	16.06.00	71,33	N	28,00	E	412	5	33,559	6,331	0,70	4,44	0,03	1
NwCC north of Stad	M. Sars	659	16.06.00	71,17	N	28,00	E	112	5	34,106	5,546	0,71	4,48	0,03	1

Table A5.3 (continued): ^{99}Tc activity concentrations in 2000

Area	Ship	Station	Sampling date	Latitude		Longitude		Depth (m)	Sampling depth (m)	Salinity	Temperature (ºC)	^{99}Tc (Bq m^{-3})	Error ± (%)	Error ± (Bq m^{-3})	Reference
NwCC north of Stad	M. Sars	660	16.06.00	70,83	N	30,00	E	381	5	33,910	5,906	0,88	4,29	0,04	1
NwCC north of Stad	M. Sars	661	16.06.00	71,00	N	30,00	E	299	5	33,757	5,828	0,90	4,32	0,04	1
NwCC north of Stad	M. Sars	687	23.06.00	70,50	N	31,22	E	187	5	33,869	5,961	0,82	4,35	0,04	1
NwCC north of Stad	M. Sars	688	23.06.00	70,40	N	31,22	E	131	5	33,456	6,136	0,94	4,35	0,04	1
1 Kershaw et al., 2004															

Table A5.4: ^{99}Tc activity concentrations in 2003

Area	Ship	Station	Sampling date	Latitude		Longitude		Depth (m)	Sampling depth (m)	Salinity	Temperature (ºC)	^{99}Tc (Bq m^{-3})	Error ± (%)	Error ± (Bq m^{-3})	Reference
Norwegian Sea / Greenland Sea	J. Hjort	423	08.06.03	75,27	N	-0,66	W	3710	1000	34,8800	-0,9410	0,06	15,1	0,01	2
Norwegian Sea / Greenland Sea	J. Hjort	423	08.06.03	75,27	N	-0,66	W	3710	1500	34,8797	-0,9411	bd	-		2
Norwegian Sea / Greenland Sea	J. Hjort	423	08.06.03	75,27	N	-0,66	W	3710	2000	34,8798	-0,9206	0,04	18,8	0,01	2
Norwegian Sea / Greenland Sea	J. Hjort	423	08.06.03	75,27	N	-0,66	W	3710	2500	34,8844	-0,8672	0,03	24,0	0,01	2
Norwegian Sea / Greenland Sea	J. Hjort	427	09.06.03	74,50	N	-10,95	W	3500	93	34,9015	0,9576	0,04	24,0	0,01	2
Norwegian Sea / Greenland Sea	J. Hjort	439	12.06.03	74,50	N	7,00	E	2450	5	35,1535	5,5730	0,08	12,6	0,01	2
Norwegian Sea / Greenland Sea	J. Hjort	439	12.06.03	74,50	N	7,00	E	2450	20	35,1528	5,5633	0,06	16,5	0,01	2
Norwegian Sea / Greenland Sea	J. Hjort	468	14.06.03	74,50	N	15,53	E	1320	70	35,1576	5,9213	0,08	12,27	0,01	2
Norwegian Sea / Greenland Sea	J. Hjort	473	15.06.03	73,50	N	19,33	E	470	100	35,1118	5,0195	0,14	8,79	0,01	2
Norwegian Sea / Greenland Sea	J. Hjort	473	15.06.03	73,50	N	19,33	E	470	320	34,9896	2,9544	0,11	12,12	0,01	2
NwCC north of Stad	J. Hjort	484	16.06.03	71,00	N	19,90	E	190	5	34,7368	7,2316	0,36	5,5	0,02	2
NwCC north of Stad	J. Hjort	487	16.06.03	70,50	N	19,99	E	120	5	34,3090	7,5031	0,50	4,9	0,02	2
Arendal / Skagerrak	-	-	01.08.03	58,42	N	8,79	E	Unknown	1	nm	nm	0,39	5,23	0,02	3
Værlandet / NwCC south of Stad	-	-	19.05.03	61,30	N	4,80	E	Unknown	1	nm	nm	1,01	4,58	0,05	3
Værlandet / NwCC south of Stad	-	-	01.12.03	61,30	N	4,80	E	Unknown	1	nm	nm	0,70	4,73	0,03	3
Rørvik / NwCC north of Stad	-	-	01.10.03	64,93	N	11,26	E	Unknown	1	nm	nm	0,74	5,02	0,04	3

highlighted=bottom sample/sample from the water column

bd=below detection limit
nm=not measured

2 Heldal (unpublished data)

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Table A5.5: ^{99}Tc activity concentrations in 2004

Area	Ship	Station	Sampling date	Latitude		Longitude		Depth (m)	Sampling depth (m)	Salinity	Temperature (ºC)	^{99}Tc (Bq m^{-3})	Error ± (%)	Error ± (Bq m^{-3})	Reference
NwCC north of Stad	G. O. Sars	553	10.11.04	62,36	N	5,20	E	175	6	33,0171	11,0322	1,32	4,4	0,06	2
NwCC north of Stad	G. O. Sars	556	10.11.04	62,73	N	4,43	E	180	6	34,1820	10,5608	1,33	4,4	0,06	2
Norwegian Sea	G. O. Sars	559	11.11.04	62,90	N	4,05	E	740	6	35,2240	9,7975	0,12	11,3	0,01	2
Norwegian Sea	G. O. Sars	562	11.11.04	63,19	N	3,40	E	1010	6	35,2054	9,7795	0,05	21,5	0,01	2
Norwegian Sea	G. O. Sars	565	12.11.04	63,66	N	2,35	E	1420	6	35,2173	9,6940	0,11	10,7	0,01	2
Arendal / Skagerrak	-	-	10.05.04	58,42	N	8,79	E	Unknown	1	nm	nm	1,03	4,53	0,05	3
Tysnes / NwCC south of Stad	-	-	24.04.04	59,92	N	5,61	E	Unknown	1	nm	nm	0,77	4,87	0,04	3
Værlandet / NwCC south of Stad	-	-	10.05.04	61,30	N	4,80	E	Unknown	1	nm	nm	0,76	4,59	0,03	3

nm=not measured

2 Heldal (unpublished data)

3 Heldal et al., 2007

Heldal, H. E., Sjøtun, K. & Gwynn, J. P. (2007) Technetium-99 in Marine Food Webs in Norwegian Seas - Results from the Norwegian RADNOR project. In Warwick, P. (Ed.) Environmental Radiochemical Analysis III.

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Table A5.6: ^{99}Tc activity concentrations in 2005

Area	Ship	Station	Sampling date	Latitude		Longitude		Depth (m)	Sampling depth (m)	Salinity	Temperature (ºC)	^{99}Tc (Bq m^{-3})	Error ± (%)	Error ± (Bq m^{-3})	Reference
Tysnes / NwCC south of Stad	-	-	16.05.05	59,92	N	5,61	E	Unknown	1	nm	nm	0,87	4,58	0,04	3
Rørvik / NwCC north of Stad	-	-	01.02.05	64,93	N	11,26	E	Unknown	1	nm	nm	0,69	4,82	0,03	3
North Sea / NwCC south of Stad	G. O. Sars	599	31.10.05	59,29	N	4,67	E	270	6	31,7798	12,3231	1,05	5,90	0,06	2
North Sea / NwCC south of Stad	G. O. Sars	683	06.11.05	60,75	N	4,11	E	315	6	30,2015	12,0658	0,81	6,24	0,05	2
Skagerrak / Kattegat	G. O. Sars	715	26.11.05	58,07	N	11,13	E	110	6	27,8031	8,8508	0,76	6,27	0,05	2
North Sea	G. O. Sars	722	27.11.05	57,00	N	7,35	E	40	6	34,5438	10,9702	1,90	5,44	0,10	2
North Sea	G. O. Sars	734	28.11.05	57,00	N	3,39	E	65	6	35,0771	9,0676	0,90	6,20	0,06	2
North Sea / East Coast of Britain	G. O. Sars	744	28.11.05	57,00	N	-0,70	W	65	6	35,0307	10,3226	0,80	6,37	0,05	2
North Sea	G. O. Sars	749	29.11.05	55,18	N	0,50	E	75	6	34,8011	9,3216	1,54	5,57	0,09	2
North Sea	G. O. Sars	751	30.11.05	53,75	N	1,00	E	25	6	34,6877	9,2663	1,92	5,45	0,10	2

nm=not measured
2 Heldal (unpublished data)
3 Heldal et al., 2007

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Table A5.7: ^{99}Tc activity concentrations in 2006

Area	Ship	Station	Sampling date	Latitude		Longitude		Depth (m)	Sampling depth (m)	Salinity	Temperature (ºC)	^{99}Tc (Bq m^{-3})	Error ± (%)	Error ± (Bq m^{-3})	Reference
Norwegian Sea	G. O. Sars	144	28.04.06	62,83	N	4,02	E	650	6	35,3555	8,8865	0,07	17,9	0,01	4
Norwegian Sea	G. O. Sars	144	28.04.06	62,83	N	4,02	E	650	101	35,3550	8,7004	0,05	25,0	0,01	4
Norwegian Sea	G. O. Sars	144	28.04.06	62,83	N	4,02	E	650	645	34,9224	-0,4923	bd	-		4
NwCC north of Stad	G. O. Sars	148	29.04.06	62,83	N	5,00	E	110	6	33,5153	5,9773	0,80	4,7	0,04	4
Norwegian Sea	G. O. Sars	149	29.04.06	63,84	N	4,00	E	1540	6	35,2424	7,9455	0,11	13,0	0,01	4
Norwegian Sea	G. O. Sars	149	29.04.06	63,84	N	4,00	E	1540	100	35,2415	7,6924	0,15	9,2	0,01	4
Norwegian Sea	G. O. Sars	149	29.04.06	63,84	N	4,00	E	1540	1531	34,9184	-0,8118	0,09	14,1	0,01	4
Norwegian Sea	G. O. Sars	158	01.05.06	66,92	N	1,49	E	1010	6	35,2502	7,3392	0,09	13,8	0,01	4
Norwegian Sea	G. O. Sars	160	02.05.06	66,92	N	7,50	E	990	6	35,2486	7,5009	bd	-		4
Norwegian Sea	G. O. Sars	166	05.05.06	68,08	N	-1,99	W	1010	6	35,1114	5,2547	0,07	21,2	0,01	4
Norwegian Sea	G. O. Sars	173	07.05.06	69,63	N	3,97	E	1010	6	35,2171	7,0390	0,12	12,5	0,02	4
Norwegian Sea	G. O. Sars	173	07.05.06	69,63	N	3,97	E	1010	100	35,1955	6,358	0,09	19,3	0,02	4
Norwegian Sea / NwCC north of Stad	G. O. Sars	178	09.05.06	69,67	N	16,00	E	240	227	35,2436	7,2566	0,06	29,6	0,02	4
NwCC north of Stad	G. O. Sars	182	09.05.06	69,66	N	16,99	E	55	6	34,3942	6,3468	0,44	5,9	0,03	4
Norwegian Sea (Komsomolets)	J. Hjort	765	23.08.06	73,72	N	13,27	E	1670	5	35,1102	8,7342	0,07	19,9	0,01	4
Norwegian Sea / Greenland Sea	J. Hjort	786	25.08.06	74,49	N	15,04	E	710	5	35,0781	9,1253	0,18	8,3	0,01	4
Norwegian Sea / Greenland Sea	J. Hjort	797	26.08.06	74,50	N	18,50	E	65	5	34,6652	5,0652	0,21	7,8	0,02	4
Norwegian Sea / Greenland Sea	J. Hjort	808	27.08.06	75,61	N	16,56	E	270	5	34,9846	8,1892	0,08	18,0	0,01	4
NwCC north of Stad	J. Hjort	833	29.08.06	70,51	N	20,01	E	160	5	34,2414	10,4651	0,44	5,4	0,02	4
Norwegian Sea	G. O. Sars	303	31.07.06	74,50	N	10,00	E	2500	5	35,0498	7,8079	0,15	8,7	0,01	4
Norwegian Sea	G. O. Sars	303	31.07.06	74,50	N	10,00	E	2500	700	34,8889	-0,5288	0,10	11,3	0,01	4
Norwegian Sea	G. O. Sars	303	31.07.06	74,50	N	10,00	E	2500	2400	34,9066	-0,8256	bd	-		4
Norwegian Sea	G. O. Sars	313	02.08.06	74,50	N	15,00	E	1710	5	35,1020	8,3618	0,06	23,2	0,01	4
Barents Sea/NwCC north of Stad	G. O. Sars	325	19.08.06	71,50	N	23,50	E	360	5	34,9756	9,8636	0,18	7,8	0,01	4
Barents Sea	G. O. Sars	342	26.08.06	74,17	N	30,40	E	330	5	34,7920	8,1895	0,09	13,8	0,01	4
Barents Sea	G. O. Sars	352	31.08.06	76,49	N	32,72	E	260	5	34,3805	4,3933	0,15	9,0	0,01	4

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Table A5.7 (continued): ^{99}Tc activity concentrations in 2006

Area	Ship	Station	Sampling date	Latitude		Longitude		Depth (m)	Sampling depth (m)	Salinity	Temperature (°C)	^{99}Tc (Bq m^{-3})	Error ± (%)	Error ± (Bq m^{-3})	Reference
Trulsvik / Skagerrak	G. M. Dannevig	177	30.04.06	58,74	N	9,22	E	126	1	25,6340	7,0350	0,47	6,7	0,03	4
Randvika, Risør / Skagerrak	G. M. Dannevig	179	30.04.06	58,70	N	9,23	E	60	1	25,5150	7,0700	0,63	5,7	0,04	4
Værlandet / NwCC south of Stad	-	-	23.11.06	61,30	N	4,80	E	Unknown	1	nm	nm	0,62	5,05	0,03	4
Espegrend / NwCC south of Stad	-	-	26.01.06	60,27	N	5,22	E	Unknown	1	32,4190	nm	1,01	4,58	0,05	5
Espegrend / NwCC south of Stad	-	-	22.02.06	60,27	N	5,22	E	Unknown	1	32,3595	nm	0,75	4,84	0,04	5
Espegrend / NwCC south of Stad	-	-	20.04.06	60,27	N	5,22	E	Unknown	1	29,9360	nm	0,67	4,77	0,03	5
Espegrend / NwCC south of Stad	-	-	19.06.06	60,27	N	5,22	E	Unknown	1	32,4170	nm	0,67	4,78	0,03	5
Espegrend / NwCC south of Stad	-	-	31.08.06	60,27	N	5,22	E	Unknown	1	29,9865	nm	0,54	4,99	0,03	5
Espegrend / NwCC south of Stad	-	-	16.11.06	60,27	N	5,22	E	Unknown	1	29,5475	nm	0,62	4,92	0,03	5
Espegrend / NwCC south of Stad	-	-	01.12.06	60,27	N	5,22	E	Unknown	1	nm	nm	0,69	6,54	0,04	2

highlighted=bottom sample/sample from the water column

bd=below detection limit
nm=not measured

2 Heldal (unpublished data)
4 NRPA, 2008. Radioactivity in the Marine Environment 2006. Results from the Norwegian National Monitoring Programme (RAME). StrålevernRapport 2008:14. Østerås: Norwegian Radiation Protection Authority.
5 Heldal, H.E. and Sjøtun, K., 2010. Technetium-99 (^{99}Tc) in annual growth segments of knotted wrack (*Ascophyllum nodosum*). Science of the Total Environment, 408, 5575-5582.

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Table A5.8: ^{99}Tc activity concentrations in 2007

Area	Ship	Station	Sampling date	Latitude		Longitude		Depth (m)	Sampling depth (m)	Salinity	Temperature (ºC)	^{99}Tc (Bq m^{-3})	Error ± (%)	Error ± (Bq m^{-3})	Reference
North Sea / NwCC south of Stad	J. Hjort	358	11.04.07	60,75	N	4,45	E	365	5	32,8462	6,3877	0,64	6,85	0,04	6
North Sea	J. Hjort	371	12.04.07	60,75	N	1,92	E	120	5	35,2884	7,7364	0,29	10,12	0,03	6
North Sea	J. Hjort	379	13.04.07	60,75	N	-0,66	W	95	5	35,3320	8,6236	0,17	14,65	0,03	6
North Sea / East Coast of Britain	J. Hjort	380	13.04.07	59,28	N	-2,23	W	67	5	34,7210	8,3455	1,49	5,61	0,08	6
North Sea	J. Hjort	390	14.04.07	59,28	N	1,00	E	105	5	35,2121	7,5934	0,36	8,28	0,03	6
North Sea / NwCC south of Stad	J. Hjort	411	15.04.07	59,28	N	5,03	E	80	5	32,6118	7,1598	0,56	7,28	0,04	6
North Sea / East Coast of Britain	J. Hjort	422	17.04.07	57,00	N	-1,46	W	60	5	34,5258	8,0831	1,38	5,62	0,08	6
North Sea	J. Hjort	433	17.04.07	57,00	N	2,97	E	62	5	35,0895	8,4488	0,61	6,92	0,04	6
North Sea / NwCC south of Stad	J. Hjort	447	19.04.07	57,99	N	6,50	E	345	5	32,2766	6,7777	0,61	7,15	0,04	6
North Sea / NwCC south of Stad	J. Hjort	448	19.04.07	57,98	N	6,49	E	345	5	32,3460	6,7530	0,51	7,94	0,04	6
Barents Sea	J. Hjort	809	08.08.07	73,19	N	18,30	E	445	5	34,7079	10,3885	0,26	7,92	0,02	6
Barents Sea	J. Hjort	809	08.08.07	73,19	N	18,30	E	445	443	35,1036	3,1181	0,14	12,3	0,02	6
Norwegian Sea (Komsomolets)	J. Hjort	817	11.08.07	73,72	N	13,26	E	1700	5	34,8642	10,1757	0,19	10,53	0,02	6
Norwegian Sea (Komsomolets)	J. Hjort	817	11.08.07	73,72	N	13,26	E	1700	1694	34,9288	-0,8748	bd	-		6
Barents Sea / NwCC north of Stad	G. O. Sars	328	18.08.07	71,36	N	27,45	E	350	6	34,4850	10,6242	0,20	9,61	0,02	6
Barents Sea / NwCC north of Stad	G. O. Sars	328	18.08.07	71,36	N	27,45	E	350	348	35,1026	4,9441	0,11	13,67	0,02	6
Skagerrak	G. M. Dannevig	180	24.04.07	58,05	N	11,05	E	121	2,5	29,8280	8,2870	0,58	6,79	0,04	6
Skagerrak	G. M. Dannevig	182	24.04.07	58,07	N	11,22	E	53	2,5	28,8590	8,1680	0,49	7,18	0,04	6
Skagerrak	G. M. Dannevig	183	24.04.07	58,55	N	10,88	E	76	2,5	29,6530	8,1790	0,45	7,58	0,03	6
Skagerrak	G. M. Dannevig	185	24.04.07	58,52	N	10,67	E	141	2,5	28,3750	8,3070	0,55	7,10	0,04	6

highlighted=bottom sample

6 NRPA, 2009. Radioactivity in the Marine Environment 2007. Results from the Norwegian National Monitoring Programme (RAME). StrålevernRapport 2009:15. Østerås: Norwegian Radiation Protection Authority.

Table A5.9: ^{99}Tc activity concentrations in 2008

Area	Ship	Station	Sampling date	Latitude		Longitude		Depth (m)	Sampling depth (m)	Salinity	Temperature (°C)	^{99}Tc (Bq m^{-3})	Error ± (%)	Error ± (Bq m^{-3})	Reference	
North Sea / NwCC south of Stad	J. Hjort	514	09.07.08	57,86	N	5,80	E	210	5	31,5033	15,4190	0,72	5,9	0,04	7	
North Sea / NwCC south of Stad	J. Hjort	514	09.07.08	57,86	N	5,80	E	210	205	35,2805	7,1998	0,29	12,2	0,04	7	
North Sea	J. Hjort	516	10.07.08	57,00	N	7,36	E	22	5	34,1202	16,0404	1,06	5,4	0,06	7	
North Sea	J. Hjort	531	11.07.08	57,00	N	2,07	E	92	5	34,9915	14,5244	0,85	5,6	0,05	7	
North Sea / NwCC south of Stad	J. Hjort	546	15.07.08	58,53	N	4,58	E	275	5	32,4660	15,2922	1,47	4,6	0,07	7	
North Sea / NwCC south of Stad	J. Hjort	557	18.07.08	59,28	N	4,83	E	178	5	29,7978	15,5441	1,17	5,0	0,06	7	
North Sea / East Coast of Britain	J. Hjort	586	21.07.08	59,28	N	-2,23	W	72	5	34,8821	11,5080	1,04	5,7	0,06	7	
North Sea / East Coast of Britain	J. Hjort	622	29.07.08	60,75	N	-0,66	W	100	5	34,5965	13,3676	1,98	4,6	0,09	7	
North Sea / NwCC south of Stad	J. Hjort	645	30.07.08	60,75	N	4,45	E	375	5	30,5515	20,1083	1,23	4,9	0,06	7	
Norwegian Sea (Komsomolets)	G. O. Sars	372	21.08.08	73,73	N	13,27	E	1695	6	34,8354	8,8357	0,19	15,1	0,03	7	
Norwegian Sea (Komsomolets)	G. O. Sars	372	21.08.08	73,73	N	13,27	E	1695	1693	34,9145	-0,8678	bd	-		7	
Norwegian Sea	G. O. Sars	374	22.08.08	74,50	N	6,99	E	1505	6	35,0562	7,4829	0,08	32,3	0,02	7	
NwCC north of Stad	G. O. Sars	404	27.08.08	71,25	N	28,73	E	400	6	34,3575	9,1502	0,35	12,0	0,04	7	X
NwCC north of Stad	G. O. Sars	404	27.08.08	71,25	N	28,73	E	400	395	35,0572	4,6477	0,16	9,0	0,01	7	X
Barents Sea	G. O. Sars	417	30.08.08	71,80	N	36,07	E	267	6	34,9732	6,6674	0,11	19,8	0,02	7	X
Barents Sea	G. O. Sars	417	30.08.08	71,80	N	36,07	E	267	264	35,0332	0,8691	0,15	13,0	0,02	7	X
Barents Sea	G. O. Sars	441/442/443	04.09.08	75,00	N	31,22	E	353	6	35,0766	5,9287	0,13	12,0	0,02	7	X
Barents Sea	G. O. Sars	441/442/443	04.09.08	75,00	N	31,22	E	353	351	35,0679	1,8594	0,16	11,4	0,02	7	X
Barents Sea	G. O. Sars	453	06.09.08	76,82	N	43,01	E	218	6	34,2444	3,0346	0,14	11,3	0,02	7	X
Barents Sea	G. O. Sars	473	12.09.08	74,53	N	41,30	E	200	6	34,9162	4,7841	0,13	12,3	0,02	7	X
Barents Sea / NwCC north of Stad	J. Hjort	647	02.09.08	70,50	N	19,99	E	122	5	34,0249	8,8054	0,34	9,1	0,03	7	X
Barents Sea	J. Hjort	654	02.09.08	71,75	N	19,73	E	263	5	34,2999	9,2328	0,25	7,9	0,02	7	X
Barents Sea	J. Hjort	658	03.09.08	72,75	N	19,52	E	398	5	34,7353	8,2996	0,26	7,0	0,02	7	X
Barents Sea	J. Hjort	667	04.09.08	74,54	N	21,65	E	155	5	34,1395	2,8255	0,10	17,1	0,02	7	X
Barents Sea	J. Hjort	675	06.09.08	78,21	N	27,17	E	313	5	32,4454	0,4062	0,10	15,9	0,02	7	X
Barents Sea	J. Hjort	677	07.09.08	78,78	N	35,96	E	238	5	33,3739	0,7575	0,20	9,7	0,02	7	X
Barents Sea	J. Hjort	677	07.09.08	78,78	N	35,96	E	238	235	34,9627	1,6179	0,13	12,4	0,02	7	X

APPENDIX 5

Table A5.9 (continued): ^{99}Tc activity concentrations in 2008

Area	Ship	Station	Sampling date	Latitude		Longitude		Depth (m)	Sampling depth (m)	Salinity	Temperature (ºC)	^{99}Tc (Bq m^{-3})	Error ± (%)	Error ± (Bq m^{-3})	Reference	
Barents Sea	J. Hjort	684	08.09.08	76,45	N	27,76	E	125	5	34,2940	2,0892	0,13	10,6	0,01	7	X
Barents Sea	J. Hjort	688	09.09.08	75,92	N	30,26	E	321	5	34,6884	5,1549	0,13	10,5	0,01	7	X
Barents Sea	J. Hjort	692	11.09.08	74,17	N	30,40	E	327	5	35,0327	6,5136	0,10	12,0	0,01	7	X
Barents Sea	J. Hjort	694	11.09.08	75,26	N	25,78	E	173	5	34,8687	5,0979	0,11	12,4	0,01	7	X
Barents Sea	J. Hjort	699	13.09.08	73,97	N	21,93	E	456	5	34,6140	4,6981	0,09	13,6	0,01	7	X
Barents Sea	J. Hjort	702	13.09.08	72,94	N	26,46	E	370	5	34,8989	7,5854	0,16	9,1	0,01	7	X
Barents Sea	J. Mayen	426	27.09.08	76,95	N	12,75	E	265	5	34,9492	6,9795	0,14	18,6	0,03	7	X
Barents Sea	J. Mayen	430	29.09.08	76,29	N	20,36	E	257	5	33,9594	2,5155	0,14	13,2	0,02	7	X
Værlandet / NwCC south of Stad	-	-	27.10.08	61,30	N	4,80	E	Unknown	1	nm	nm	0,48	8,4	0,04	7	

highlighted=bottom sample
X =Analysed during this master project
bd=below detection limit
nm=not measured

7 NRPA, 2011. Radioactivity in the Marine Environment 2008 and 2009. Results from the Norwegian National Monitoring Programme (RAME). StrålevernRapport 2011:4. Østerås, Norwegian Radiation Protection Authority.

APPENDIX 5

Table A5.10: ^{99}Tc activity concentrations in 2009

Area	Ship	Station	Sampling date	Latitude		Longitude		Depth (m)	Sampling depth (m)	Salinity	Temperature (ºC)	^{99}Tc (Bq m^{-3})	Error ± (%)	Error ± (Bq m^{-3})	Reference	
Barents Sea / NwCC north of Stad	J. Hjort	68	05.03.09	70,50	N	20,00	E	140	5	34,1885	4,8134	0,25	7,0	0,02	7	X
Barents Sea	J. Hjort	78	05.03.09	72,50	N	19,56	E	387	5	35,0716	5,6558	0,10	11,4	0,01	7	X
Barents Sea	G. O. Sars	464	26.08.09	73,96	N	21,85	E	467	6	35,0404	7,1546	0,11	12,1	0,01	7	X
Barents Sea	G. O. Sars	474	28.08.09	74,81	N	18,02	E	294	6	34,4459	3,8195	0,11	17,8	0,02	7	
Barents Sea	G. O. Sars	480	31.08.09	76,22	N	18,57	E	252	6	34,4527	4,3070	0,12	10,2	0,01	7	X
Barents Sea	G. O. Sars	493	03.09.09	72,02	N	15,50	E	672	6	34,6304	10,9624	0,19	8,3	0,02	7	X
NwCC north of Stad	G. O. Sars	TP18	09.10.09	69,37	N	14,83	E	1481	6	nm	nm	0,06	47,9	0,03	7	
Norwegian Sea (Komsomolets)	J. Hjort	479-482	16.08.09	73,72	N	13,28	E	1681	5	34,8236	9,5933	0,14	9,2	0,01	7	
Norwegian Sea (Komsomolets)	J. Hjort	479-482	16.08.09	73,72	N	13,28	E	1685	1680	34,8911	-0,8690	0,03	26,4	0,01	7	
Barents Sea	J. Hjort	533	03.09.09	76,82	N	43,03	E	221	5	34,2221	3,0173	0,16	8,3	0,01	7	
Barents Sea	J. Hjort	549	07.09.09	76,62	N	34,46	E	182	5	34,1048	2,9371	0,16	8,2	0,01	7	
Barents Sea	J. Hjort	571	13.09.09	74,53	N	41,30	E	204	5	34,8082	4,1814	0,12	9,9	0,01	7	
Barents Sea / NwCC north of Stad	J. Hjort	576	17.09.09	71,00	N	30,94	E	277	5	34,4081	8,7733	0,28	7,0	0,02	7	
Barents Sea	J. Hjort	591	19.09.09	75,00	N	31,21	E	351	5	35,0371	6,2303	0,10	12,5	0,01	7	
Barents Sea	J. Hjort	610	24.09.09	73,50	N	29,14	E	405	5	34,9503	7,5476	0,15	9,3	0,01	7	
Barents Sea	J. Hjort	624	28.09.09	72,94	N	26,00	E	374	5	34,9741	7,3038	0,21	7,6	0,02	7	X

APPENDIX 5

Table A5.10 (continued): ^{99}Tc activity concentrations in 2009

Area	Ship	Station	Sampling date	Latitude		Longitude		Depth (m)	Sampling depth (m)	Salinity	Temperature (ºC)	^{99}Tc (Bq m^{-3})	Error ± (%)	Error ± (Bq m^{-3})	Reference	
Barents Sea	J. Hjort	630	29.09.09	71,80	N	36,07	E	275	5	35,0126	5,9334	0,13	10,5	0,01	7	X
Barents Sea	J. Mayen	530/434*	11.09.09	76,93	N	12,75	E	257	5	34,8187	7,0507	0,10	12,1	0,01	7	X
Barents Sea	J. Mayen	558/435	18.09.09	79,65	N	15,44	E	138	5	33,9923	4,3673	0,09	13,6	0,01	7	X
Barents Sea	J. Mayen	569/436	20.09.09	81,27	N	22,93	E	210	5	30,9728	-1,6096	0,07	15,1	0,01	7	X
Barents Sea	J. Mayen	574/437	22.09.09	78,60	N	25,17	E	157	5	32,6537	0,192	0,08	14,6	0,01	7	X
Barents Sea / NwCC north of Stad	J. Mayen	438	26.09.09	71,33	N	22,47	E	429	5	nm	nm	0,11	12,9	0,01	7	X
Værlandet / NwCC south of Stad	-	-	16.11.09	61,30	N	4,80	E	Unknown	1	nm	nm	0,43	7,6	0,03	7	

highlighted=bottom sample

X =Analysed during this master project

TP = Tilførselsprogrammet

*Grabbstasjonsnummer

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7 NRPA, 2011. Radioactivity in the Marine Environment 2008 and 2009. Results from the Norwegian National Monitoring Programme (RAME). StrålevernRapport 2011:4. Østerås, Norwegian Radiation Protection Authority.

APPENDIX 5

Table A5.11: ^{99}Tc activity concentrations in 2010

Area	Ship	Station	Sampling date	Latitude		Longitude		Depth (m)	Sampling depth (m)	Salinity	Temperature (ºC)	^{99}Tc (Bq m^{-3})	Error ± (%)	Error ± (Bq m^{-3})	Reference	
North Sea / NwCC south of Stad	J. Hjort	TP10 / 498	05.07.2010	59,03	N	4,71	E	276	5	34,1547	11,3	0,41	6,3	0,03	8	X
North Sea / NwCC south of Stad	J. Hjort	TP9 / 503	06.07.2010	57,78	N	7,10	E	400	5	31,5147	13	0,40	6,3	0,03	8	X
Skagerrak	J. Hjort	22 / 505	07.07.2010	57,98	N	8,09	E	466	5	29,0396	15,5	0,39	6,3	0,02	8	X
Skagerrak	J. Hjort	19 / 506	07.07.2010	58,11	N	8,04	E	210	5	30,2040	13,8	0,38	6,6	0,02	8	X
Skagerrak	J. Hjort	26 / 507	08.07.2010	57,85	N	8,20	E	526	5	28,9379	15,8	0,38	6,3	0,02	8	X
Skagerrak	J. Hjort	28 / 508	08.07.2010	57.65	N	8,33	E	219	5	29,4478	16,4	0,32	6,7	0,02	8	X
Skagerrak	J. Hjort	X	08.07.2010	57,22	N	8,54	E	unknown	5	31,36	15,8	0,32	6,6	0,02	8	X
North Sea	J. Hjort	29 / 509	08.07.2010	57,00	N	7,36	E	42	5	32,9573	14,8	0,38	6,4	0,02	8	X
North Sea	J. Hjort	30 / 516	10.07.2010	57,17	N	2,09	E	84	5	35,0467	13,8	0,43	6,3	0,03	8	X
North Sea / NwCC south of Stad	J. Hjort	TP26 / 535	13.07.2010	57,93	N	4,90	E	101	5	34,3867	13,6	0,27	7,0	0,02	8	X
North Sea	J. Hjort	13 / 545	15.07.2010	58,42	N	2,55	E	72	5	35,0495	13,9	0,33	6,6	0,02	8	X
North Sea	J. Hjort	14 / 549	17.07.2010	58,41	N	1,13	E	138	5	35,145	13,6	0,31	6,8	0,02	8	X
North Sea / NwCC south of Stad	J. Hjort	TP11 / 555	18.07.2010	58,92	N	3,84	E	276	5	33,9516	13,4	0,35	6,5	0,02	8	X
North Sea	J. Hjort	11 / 576	19.07.2010	59,28	N	0,67	E	136	5	35,2307	13,3	0,14	11,6	0,02	8	X
North Sea / East Coast of Britain	J. Hjort	10 / 586	19.07.2010	59,28	N	-2,23	W	98	5	34,722	11,8	0,77	5,5	0,04	8	X
North Sea	J. Hjort	6 / 596	26.07.2010	60,00	N	1,00	E	123	5	35,1137	13,9	0,12	10,7	0,01	8	X
North Sea / NwCC south of Stad	J. Hjort	3 / 608	27.07.2010	60,75	N	3,51	E	323	5	33,2310	14,5	0,28	6,9	0,02	8	X
North Sea	J. Hjort	TP27 / 615	29.07.2010	60,83	N	1,33	E	142	5	34,8131	13,7	0,20	8,2	0,02	8	X
North Sea	J. Hjort	1 / 624	31.07.2010	60,76	N	-0,68	W	109	5	35,2444	12,4	0,15	9,2	0,01	8	X

Table A5.11 (continued): ^{99}Tc activity concentrations in 2010

Area	Ship	Station	Sampling date	Latitude		Longitude		Depth (m)	Sampling depth (m)	Salinity	Temperature (°C)	^{99}Tc (Bq m^{-3})	Error ± (%)	Error ± (Bq m^{-3})	Reference	
North Sea / NwCC south of Stad	J. Hjort	4 / 627	01.08.2010	60,75	N	4,45	E	372	5	31,3076	14,7	0,33	6,5	0,02	8	X
NwCC north of Stad	J. Hjort	1	19.01.2010	62,37	N	5,20	E	160	5	32,5532	5,4	0,27	8,1	0,02	2	
Norwegian Sea	J. Hjort	8	20.01.2010	63,19	N	3,39	E	1005	5	35,3221	8,7	0,20	8,8	0,02	2	
Norwegian Sea	J. Hjort	22	23.01.2010	69,14	N	11,95	E	1507	5	35,209	7,3	0,12	13,7	0,02	2	
Norwegian Sea / NwCC north of Stad	J. Hjort	28	24.01.2010	68,43	N	14,01	E	109	5	34,0639	5,8	0,23	8,8	0,02	2	
Barents Sea / NwCC north of Stad	J. Hjort	29	25.01.2010	70,50	N	20,00	E	119	5	34,2918	6,0	0,21	8,8	0,02	2	
Barents Sea	J. Hjort	39	28.01.2010	72,50	N	19,57	E	385	5	35,1184	6,4	0,15	11,5	0,02	2	

X =Analysed during this master project

TP= Tilførselsprogrammet

X=extra station

2 Heldal (unpublished data)
8 This study

APPENDIX 6: Fundamentals and definitions / Statistics of counting

Fundamentals and definitions

Nuclide: ${}^{A}_{Z}X$, for example ${}^{99}_{43}Tc$, X=element, Z=proton number, N=neutron number, A=mass number A=Z+N, z=electron number. Neutral atom: Z=z

Stable nuclides have a stable neutron to proton–ratio (N/Z-ratio) over time, while unstable nuclides (radionuclides) change nucleus composition over time. Ionizing radiation is emitted and N/Z-ratio changes until stability is reached.

Isotopes: nuclides with equal proton number (Z) (same place in the periodic table).

Radionuclide: radioactive nuclides are termed radionuclides

Ionizing radiation: The highly energetic α – particles, β – particles and γ – rays (short – wavelength electromagnetic radiation) have sufficiently high energy to knock out one or more electrons from atoms or molecules in matter (i.e. cause ionization). Ionizing radiation can cause severe damage to the molecular structure of a substance. In biological tissue the effect of such radiation can be very serious due to ionization or excitation of water molecules inducing free radicals (highly reactive species) that can damage membranes, tissues, enzymes, proteins and DNA / RNA.

Radioactive decay: unstable radionuclides will decay with time and a daughter nuclide is formed. The disintegration follows a first order kinetic expression. Radioactivity is a random process. The decay rate, A, is a measure of the number of disintegrations per unit time.

$A = - dN/dt$

The decay rate is proportional to the number of radioactive atoms, N, present. If the number of radioactive nuclei and the number of decays per unit time is great enough to allow a statistical treatment, then

$- dN/dt = \lambda N$

where λ is the decay constant.

If the time Δt during which ΔN atoms decay is very small compared to $t_{1/2}$ (< 1 %), we can write, $A = \Delta N/\Delta t = \lambda N$

Upon integration the general equation for simple radioactive decay becomes

$N = N_0 \, e^{-\lambda t}$

where N_0 is the number of nuclei present at some original time t_0. (Exponential decay)

Since A is proportional to N, the equation can be rewritten as

$A = A_0 \, e^{-\lambda t}$

(Choppin et al., 2002)

Half-life, $t_{1/2}$: The half-life is the time required for half of the radionuclides to decay.

$A/A_0 = N/N_0 = ½ = e^{-\lambda t1/2}$

and thus

$t_{1/2} = \ln 2 / \lambda = 0.693 / \lambda$

Activity, A: The SI unit for activity is Becquerel (Bq), disintegrations per second, and the activity is given in reciprocal seconds, s^{-1} (Choppin et al., 2002).

$1\ \mathrm{Bq} = 1\ (\mathrm{disintegration})\ s^{-1}$

Specific activity, a: Specific activity is defined as the activity (A) per unit mass (w) of an isotope. The SI unit of specific activity is Bq kg^{-1}. For practical purposes it is often given as Bq g^{-1}.

Example: the specific activity of ^{99}Tc is given as:

$$a = \frac{A}{w} = \frac{\ln 2 \cdot N_A}{t_{1/2} \cdot M_w} = \frac{\ln 2 \cdot (6.02 \cdot 10^{23} mol^{-1})}{213000 y \cdot 31536000 \sec / y \cdot 99 g / mol} = 6.36 \cdot 10^8 \, Bq / g = 636 kBq / mg$$

Where

N_A: Avogadro’s number ($6.02 \cdot 10^{23}$ mol^{-1})

$t_{1/2}$: the half life (in seconds)

M_w: the molecular mass or atomic mass (g mol^{-1})

Activity concentration is given in Bq m^{-3} or Bq L^{-1} (Choppin et al., 2002).

For technetium-99 ($t_{1/2} = 2.1 \cdot 10^5$ year) we have:

$1\ g = 6.36 \cdot 10^8\ Bq = 6.083 \cdot 10^{21}$ atoms

$1\ Bq = (6.36 \cdot 10^8\ Bq/g)^{-1} = 1.572 \cdot 10^{-9}\ g = 9.554 \cdot 10^{12}$ atoms

Atomic mass, $M_w = 99$ g/mol

$1\ mol = 99\ g = (99 g \cdot (6.36 \cdot 10^8\ Bq/g)) = 6.3 \cdot 10^{10}$ Bq

Avogadro’s number, $N_A = 6.022 \cdot 10^{23}\ mol^{-1}$

Numbers of atoms (N) per gram:

$N = n \cdot N_A = (m/M_w) \cdot N_A = (1g/99g/mol) \cdot 6.022 \cdot 10^{23}$ atoms/mol = $6.083 \cdot 10^{21}$ atoms/g

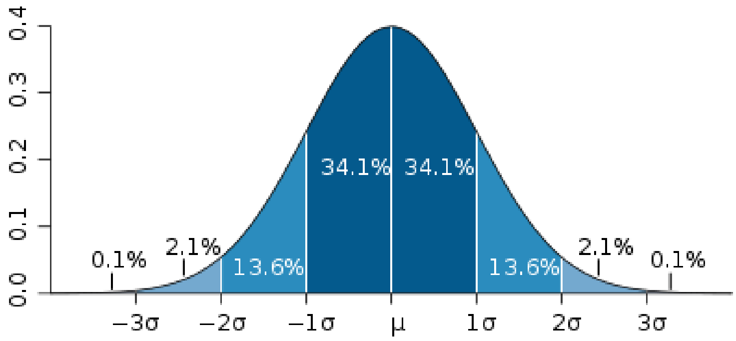
$N = n \cdot N_A = (m/M_w) \cdot N_A = (1.572 \cdot 10^{-9}$ g/99g/mol$) \cdot 6.022 \cdot 10^{23}$ atoms/mol = $9.554 \cdot 10^{12}$ atoms/g

Statistics of counting

Radioactive disintegration is a statistically random process. It is impossible to predict if or when a nucleus will decay during a particular time interval. We can only discuss the probability of the nucleus' decay. For an individual nucleus, the probability of decay to occur during a time interval, t, is given by $(1 - e^{-\lambda t})$.

Since disintegration is a random process, the uncertainty in the measurement is reduced by sufficient counting time, providing a large number of counts. For events having only two possible outcomes, the binominal distribution law applies. Radioactive decay fits into this category since a nucleus has only two possible outcomes during the time of observation: 1) decay or 2) not decay. A simplified model based on the Poisson distribution can be used when the probability of a single event is very low compared to the total number of cases. This is valid for most cases of radioactive decay since the probability of one atom decaying out of a sample of maybe 10^{18} or more atoms, is small. For low values of measured counts, the Poisson distribution is not symmetrical around the mean value, but distorted toward the right side (higher value) of the mean value. If the number of measurements recorded is high (n>100), the Gaussian distribution, which is an even simpler model, can be used with little error. The Gaussian distribution, "the normal curve", is symmetrical about the mean value, and is most often used for describing radioactive decay. Uncertainty is expressed by the variance (σ^2) or by the standard deviation (σ). The smaller the variance, the smaller the uncertainty about the mean is (and the narrower Gaussian curve). Using the Poisson distribution, we can estimate the uncertainty from the mean value, $\bar{x}$, when the number of measurements is large. The equation used to calculate the standard deviation in the case of Poisson distribution is then: $\sigma = (\bar{x})^{1/2}$(Ehmann and Vance, 1991).

For the Gaussian distribution 68.3% of the measurements will be within ± 1 σ of the mean value (estimate of the true value, μ), and 95.5 % will be within ± 2 σ. Figure 1 shows the Gaussian distribution with standard deviation.



Figur 10: The Gaussian distribution with standard deviation. 68.3% of the measurements will be within ± 1 σ of the mean value (estimate of the true value, μ), and 95.5 % will be within ± 2 σ. (Source: http://en.wikipedia.org/wiki/File:Standard_deviation_diagram.svg)

The arithmetic mean $\bar{x}$:

$$\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i$$

The more observations, the closer $\bar{x}$ will be to the true value, μ.

The Poisson distribution is given by: $P_n = \frac{\mu^x e^{-\mu}}{x!}$

The Gaussian distribution is given by: $G_n = \frac{1}{\sqrt{2\pi\mu}} e^{-(x-\mu)^2/2\mu}$

References

CHOPPIN, G. R., RYDBERG, J. & LILJENZIN, J. O. (2002) *Radiochemistry and nuclear chemistry,* [Oxford], Butterworth-Heinemann.

EHMANN, W. D. & VANCE, D. E. (1991) *Radiochemistry and nuclear methods of analysis*, John Wiley & Sons, Inc.