Iodine Isotopes and their Species in Surface Water from the North Sea to the Northeastern Atlantic Ocean

PENG HE
Abstract


Huge amounts of anthropogenic $^{129}\text{I}$ have been and still are released to the environment through liquid and gaseous discharges from the nuclear fuel reprocessing facilities worldwide and in particular the ones in Europe. Most of this $^{129}\text{I}$ signal has been accumulated in the marine environment which plays a major role in the iodine natural pool. In this thesis, an overview of available $^{129}\text{I}$ concentrations in waters of the oceans and marginal seas together with new data about $^{129}\text{I}$ and $^{127}\text{I}$ spatial distribution in surface seawater along a transect between the North Sea and the northeastern Atlantic Ocean are presented. After comprehensive chemical separation, the concentrations of iodine isotopes ($^{127}\text{I}$ and $^{129}\text{I}$) and their species (iodide and iodate) were analysed using accelerator mass spectrometry and inductively-coupled plasma mass spectrometry. The results show that, generally, changes in the $^{127}\text{I}$ and $^{129}\text{I}/^{127}\text{IO}_3^-$ are comparable to data from other marine waters which are related to natural distribution patterns. A considerable variation of $^{129}\text{I}$ along the transect is observed with the highest values occurring in the eastern English Channel and relatively low values obtained in the northeastern Atlantic Ocean. Inventory estimations of $^{129}\text{I}$ in the North Sea and the English Channel are 147 kg and 78 kg, respectively, where more than 90% resides in the Southern Bight and the eastern English Channel. Iodate is the dominant iodine species for both $^{127}\text{I}$ and $^{129}\text{I}$ in most seawater samples from the North Sea to the Atlantic Ocean. $^{129}\text{I}$ species variability suggests a slow process of $^{129}\text{I}$ oxidation in the open sea. It takes at least 10 years for the $^{129}\text{I}/^{129}\text{IO}_3^-$ pair to reach their natural equilibrium as the water is transported from the English Channel. The results suggest a main transport of $^{129}\text{I}$ from the western English Channel via the Biscay Bay into the northeastern Atlantic Ocean. Further, high $^{129}\text{I}/^{127}\text{I}$ and distinctive $^{129}\text{I}/^{129}\text{IO}_3^-$ values south of 40°N indicate possible contribution of $^{129}\text{I}$ through Mediterranean Outflow Water. The environmental radioactive impact of $^{129}\text{I}$ and possible applications in ecosystem studies are also discussed.

Keywords: iodine isotopes, 129I, 127I, oceans, North Sea, speciation, Atlantic Ocean, English Channel, Celtic Sea, AMS, iodine chemistry, geochemistry

Peng He, Uppsala University, Department of Earth Sciences, LUVAL, Villav. 16, SE-752 36 Uppsala, Sweden.

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In memory of my Grandma Zhang,
Dedicated to my parents
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


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I have written first draft of all papers, with other authors contributing to further interpretations and discussions. I made all the sampling and chemical preparation. I also performed data evaluation, calculation and modeling.
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1. Introduction

1.1 General background

Iodine is a trace element which ubiquitously exists in the Earth’s surface environment (i.e. atmosphere, lithosphere, hydrosphere and biosphere). Due to its biophilic nature, iodine is easily taken up by organisms and therefore tends to be enriched in organic matters (Vinogradov, 1953). Iodine is found in high concentrations in marine seaweed and in some brown algae, the concentration by dry weight measurement can reach > 10\(^{-3}\) g·g\(^{-1}\) (Hou and Yan, 1998), while in terrestrial plants, the concentrations are normally lower (Fuge and Johnson, 1986). As a nutrient element, iodine is indispensable and essential to all mammals. Many trace elements in the environment have a close relation to the human health and nutrition. Linkage between iodine deficiency disorders (IDD) such as goiter and intake amount of iodine in human daily diet have evoked enormous attentions to this element. In addition, recent studies on atmospheric chemistry showed that iodine plays a significant role in the depletion of ozone and in aerosol particles for cloud nucleation, which in turn have a direct impact on global climate change (Solomon et al., 1994; O'Dowd et al., 2002; von Glasow, 2006).

Although iodine has long been recognized as an important environmental element, data on distribution of iodine in natural environments were generalized and poorly described in early studies. As one of the most important reservoirs, the oceans contain more than 70% of the mobile iodine in the Earth’s surface environment (Wong, 1991; Alfimov, 2005). Iodine in some sparse seawater samples collected in the Atlantic, Pacific, Arctic and Indian Oceans, as well as the Mediterranean and Red Seas, were discussed in the early decades of the last century (Reith, 1930; Barkley and Thompson, 1960). These studies reported a rather constant concentration of total iodine in oceans, but varying proportions of iodate with location and depth. The first extensive survey of iodine and its speciation in the whole Pacific Ocean was conducted by a Japanese group. They found a latitudinal variation of iodide in the surface of the Pacific seawaters and they related this feature to the high biological productivity. In the meantime, they also observed elevated iodide concentration in bottom waters (Tsunogai, 1971; Tsunogai and Henmi, 1971). Later, a systematic investigation of iodine concentration in near surface waters was deployed along a transect across the Atlantic Ocean, which presented a rather similar feature in terms of meridional distribution of io-
dine (including its species) as that observed in the Pacific Ocean (Truesdale et al., 2000).

The only long-lived radioactive isotope of iodine, $^{129}$I ($T_{1/2} = 15.7$ Myr), is mainly introduced into the environment anthropogenically through nuclear activities that started in the 1940s. As a result, the $^{129}$I/$^{127}$I was increased to at least two orders of magnitude higher than the pre-nuclear era globally. Because of its long half-life and low radiation energy, $^{129}$I was suggested as a potential tracer of iodine geochemistry (Edwards, 1962). Thereafter some environmental samples were collected for $^{129}$I analysis (Oliver et al., 1982; Fabryka-Martin et al., 1987). The Chernobyl accident, one of the most serious nuclear accidents, occurred on 26 April 1986, and released many types of anthropogenic radioactive isotopes including $^{129}$I into the environment. Thus measurements of some soil, rainwater and animal thyroid samples were reported in order to assess the impact of iodine isotopes ($^{129}$I and $^{131}$I) in the vicinity environment of the Chernobyl region (Paul et al., 1987b; Kutschera et al., 1988; VanMiddlesworth and Handl, 1997; Hou et al., 2003; Michel et al., 2005). Release of $^{129}$I from the recent Japan Fukushima Dai-ichi nuclear accident on 11 March 2011 was estimated by Hou et al. (Hou et al., 2013).

Awareness of potential environmental hazards as a result of huge $^{129}$I releases from the nuclear fuel reprocessing facilities (NRFs) led to extensive data collection in the surrounding areas of major NRFs such as Hanford (USA), Tokaimura (Japan) (Muramatsu and Ohmomo, 1986), Karlsruhe (WAK, Germany) (Robens et al., 1988), Sellafield (UK), La Hague (France) (Edmonds et al., 1998) and Russian facilities (e.g. Mayak, Seversk and Zheleznogorsk). Estimation of early marine discharges of $^{129}$I from La Hague and Sellafield was evaluated by Raisbeck et al. based on times series analysis of $^{129}$I/$^{127}$I in seaweeds (Raisbeck et al., 1995). Since then, many studies have been carried out using $^{129}$I as an oceanographic tracer in many $^{129}$I-contaminated regions (e.g. English Channel, Irish Sea, North Sea, Arctic Ocean, etc.) (Beasley et al., 1998; Cooper et al., 1998; Buraglio et al., 1999; Smith et al., 1999; Hou et al., 2000a; Cooper et al., 2001; Edmonds et al., 2001; Alfimov et al., 2004b; Alfimov et al., 2004c; Smith et al., 2005; Hou et al., 2007; Schnabel et al., 2007; Orre et al., 2010; Hansen et al., 2011b; Smith et al., 2011; Yi et al., 2012b; Yi et al., 2013).
1.2 Objectives of this thesis

The use of chemical tracers (natural and anthropogenic) has expanded our understanding of circulation patterns and ventilation rates in the oceans. Numerous studies have, however, shown that we are still far away from complete understanding of most oceanic processes and further development in tracer technology can, without doubt, substantially increase our knowledge.

Investigations of $^{129}$I geochemical behavior have been carried out by the Uppsala group for years. These studies were mainly focused on $^{129}$I in the marine environment at high latitudes in the Northern Hemisphere, including the Arctic Ocean (Buraglio et al., 1999), the Nordic Seas (Alfimov et al., 2004) and the Baltic Sea (Yi et al., 2010). In the thesis presented here, a focus is given on exploring distribution of iodine isotopes ($^{127}$I and $^{129}$I) and their species (iodide and iodate) along a transect across the North Sea passing by the English Channel and into the northeastern Atlantic Ocean. The objectives of this thesis are:

1. Reviewing of the global distribution of $^{129}$I in the oceans and identifying regional variability.
2. Revealing temporal evolution of $^{129}$I and its species in surface water of the North Sea in comparison to earlier data.
3. Documenting distribution and sources of iodine isotopes ($^{129}$I and $^{127}$I) and their species (iodide and iodate) in the surface waters of the English Channel, the Celtic Sea and the northeastern Atlantic Ocean.
4. Exploring the potential of $^{129}$I species inter-conversion as a tracer of surface water sources in the northeastern Atlantic.
5. Assessing environmental impact and future effects on the marine ecological systems.

Before going into details of the thesis work, a summary of iodine chemistry and distribution in the environment is given below.

1.3 Stable iodine ($^{127}$I) and its sources

Iodine is a redox sensitive element with oxidation states of -1, 0, +1, +3, +5 and +7. There are 37 known isotopes of iodine in which $^{127}$I is the only stable one. Although iodine is the least abundant halogen element, it is widespread in Earth’s crust with an average abundance of 0.45 mg/kg (Hou et al., 2009b). Most iodine is found in igneous and sedimentary rocks, though in low concentrations (0.24-4 mg/kg) (Fuge and Johnson, 1986). However, a major part of iodine is bound in rocks, sediments and soils. Only a small
amount occurs in the marine pool and the global cycle (Fuge and Johnson, 1986; Moreda-Pineiro et al., 2011).

The ocean is the major mobile iodine pool that interacts with land, atmosphere and biosphere. Some studies suggested that the main mode of iodine transport from sea to land is through wet (precipitation) deposition (Truesdalea and Jones, 1996; López-Gutiérrez et al., 2001; Reithmeier et al., 2010). Therefore it seems reasonable to draw a general pattern of decreasing iodine content with increased distance from oceans, which coincides with the prevalence of IDD (Selinus, 2005). However, this hypothesis remains doubtful since some counterexamples have been reported (Krupp and Aumann, 1999). Bearing in mind that iodine is easily incorporated in organic matters and trapped by soils and sediment, distribution of iodine on land is thus also affected by the type of soils (Gerzabek et al., 1999; Yoshida, 1999). In addition, iodine may be derived from erosion of bedrock (Hou et al., 2009b).

Emission of iodocarbons from the ocean surface provides a major source of atmospheric iodine which eventually contributes to reactive iodine in the marine boundary layer (MBL). Methyl iodide (CH$_3$I) is considered to be the principal species while recently, high concentration of molecular iodine (I$_2$) was reported in a coastal marine environment (Chatfield and Crutzen, 1990; Saiz-Lopez et al., 2006; Küpper et al., 2008). Accordingly, microalgae (phytoplankton) and macroalgae (seaweeds) appear to play a dominant role in the open sea and coastal areas, respectively (Carpenter, 2003). On land, large iodine emissions from wetlands, vegetation and soils are most important (Sive et al., 2007).

Some anthropogenic sources of iodine are related to agricultural and industrial activities. About 5% of methyl iodide in the atmosphere is estimated to be derived from emission of rice paddies (Redeker et al., 2000). The use of soil fumigant in pest control may also add iodine into the environment (Aldahan et al., 2009). Combustion of fossil fuel provides another important source of iodine to the atmosphere due to relatively high average concentrations of iodine in coal and petroleum, 4 mg/kg and 1 mg/kg respectively (Block and Dams, 1974; Valkovic, 1978). Additionally, application of iodine as a disinfectant makes municipal wastewater treatment plants an important source of iodine in surface waters (Moreda-Pineiro et al., 2011). However, the contribution of iodine from anthropogenic sources inland is much less when compared to natural sources of marine origin and therefore, could be considered negligible (Chameides and Davis, 1980; Carpenter, 2003).

1.4 Radioactive iodine (I$^{129}$) and its sources

The only naturally occurring long-lived ($T_{1/2} = 15.7$ Myr) radioisotope of iodine, I$^{129}$, which is a beta emitter with relatively low energy radiation (154.4 keV, $E_{\beta_{\max}}$), is an important soluble fission product in spent nuclear
fuel. $^{129}$I can be naturally produced by spallation of xenon (Xe) induced by interaction with cosmic rays in the upper atmosphere, as well as from spontaneous fission of $^{238}$U and thermal neutron-induced fission of $^{235}$U inside the Earth (Snyder et al., 2010). Neutron bombardment ($^{130}$Te) and neutron capture ($^{128}$Te) of tellurium isotopes are, to a lesser extent, another natural source of $^{129}$I (Hou et al., 2009b). The collective $^{129}$I natural flux contributes to a $^{129}$I/$^{127}$I ratio of $10^{-13}$ to $10^{-12}$ prior to human nuclear activities (Broecker and Peng, 1982; Fabryka-Martin et al., 1985; Fehn, 1986; Moran et al., 1998; Fehn et al., 2007) and the total natural inventory of $^{129}$I is therefore estimated to be 100-260 kg (Fabryka-Martin et al., 1985; Raisbeck and Yiou, 1999; Snyder et al., 2010), which is insignificant when compared to the anthropogenic sources (Figure 1.1).

Since the start of the nuclear era in the 1940s, $^{129}$I has been overwhelmingly introduced into the environment by a variety of anthropogenic sources, including: 1) aboveground nuclear weapons tests, 2) nuclear accidents, 3) discharges from nuclear fuel reprocessing plants and possibly 4) the nuclear power plants during routine operation. Aboveground nuclear weapons testing, which peaked in the 1960s, has released various radionuclides into the stratosphere, thus eventually contributing to a global fallout, particularly in the Northern Hemisphere (Wilkins, 1989; Snyder and Fehn, 2004; (Reithmeier et al., 2006). These tests have introduced 57-135 kg of $^{129}$I into the environment (NCRP, 1983; Wagner et al., 1996; Raisbeck and Yiou, 1999). Amounts of $^{129}$I released by some nuclear accidents are difficult to estimate, but it is considered insignificant, since no evidence of any enhanced $^{129}$I has been found in surrounding areas of Windscale (10 Oct. 1957) (Gallagher et al., 2005) and Three Mile Island (28 Mar. 1979) (Moran et al., 2002b; Gallagher et al., 2005). Estimations of $^{129}$I emitted by the most serious nuclear accident ever, the Chernobyl accident (26 Apr. 1986), is between 1.3 and 6 kg, which is even 10 times lower than releases from nuclear weapons testing (Paul et al., 1987; Aldahan et al., 2007b). Comparable releases of $^{129}$I (1.2 kg) was estimated from the recent nuclear accident in Japan (12 Mar. 2011, Fukushima) (Hou et al., 2013). $^{129}$I release from the nuclear power plants is insignificant (Hou et al., 2002; He et al., 2010). In addition, because of the highly mobile and soluble nature of iodine, dumping of nuclear radioactive waste could be another potential $^{129}$I source to the marine deep layer. However, previous surveys on radioactive waste dumping sites in the Atlantic and Pacific Oceans did not show any abnormal concentration of $^{129}$I that is above the expected background natural level (Povinec et al., 2000; Cooper et al., 2001). Thus at present, $^{129}$I from radioactive waste dumping source is considered negligible. It is worth mentioning that an estimated 68 tons of $^{129}$I were produced in routine nuclear power plants operation, mostly waiting for future reprocessing (Hou et al., 2009b).
The function of the nuclear reprocessing facilities (NRFs) is to extract fissionable plutonium (Pu) from irradiated nuclear fuel since the 1940s. Some of them were decommissioned (e.g. Hanford and Marcoule) and some are still operating (e.g. Sellafield and La Hague) for commercial use. These NRFs have discharged more than 95% of total $^{129}$I inventory into the Earth’s surface environments (Figure 1.1). Among them, around 90% of $^{129}$I is released from the two major European NRFs Sellafield and La Hague, which are located in the United Kingdom and France, respectively. Until 2011, these two NRFs have together discharged 5400 kg and 250 kg $^{129}$I directly to marine environment and the atmosphere, respectively (He et al., 2013; AREVA; Monitoring our Environment, Sellafield Annual Report). The discharge rate of $^{129}$I from these two facilities increased and remained high after 1990 and peaked in 1997, but declined slightly during the past 10 years (Figure 1.2).
Figure 1.2: Annual marine and atmospheric releases from (a) Sellafield (UK) and (b) La Hague (France) between 1966 and 2011 (literatures refer to the text).

Marcoule (France) is another major European NRF that has released 180 and 75 kg of $^{129}$I to the atmosphere and Rhone river, respectively (Hou et al., 2009b). For comparison, only 1.1 kg of $^{129}$I was released from the Karlsruhe NRF (WAK), which is located in Germany and was decommissioned in 1987 (Robens et al., 1988). The largest gaseous releases of $^{129}$I were from the Hanford NRF (USA), ranging at 300 kg during its operation from 1944 to 1988 (HHIN; Moran et al., 1998). This discharge is even greater than that of the total amount by Sellafield and La Hague. Furthermore, total gaseous $^{129}$I released from Savannah River NRF and some major former Soviet NRFs was estimated by an atmospheric transport box model (Reithmeier et al., 2010). The outcome suggested that about 41 and 215 kg of $^{129}$I were emitted to the atmosphere during their operation times for Savannah River NRF and former Soviet NRFs (including Mayak, Seversk and Zheleznogorsk) respectively. In Asia, a Japanese NRF located at Tokai, has released about 1.0 kg of $^{129}$I to the environment (JAEA; Shinohara, 2004). Release records of the other Asian NRFs (i.e. in China and India) are, however, not well documented.

1.5 Applications of $^{129}$I and its species

Implementation of the highly sensitive analytical technique of accelerator mass spectrometry (AMS) allowed determination of ultra-low $^{129}$I/$^{127}$I values in pre-nuclear era materials. The present detection limit of AMS and the long half-life of $^{129}$I have made the technique a powerful tool in radiometric dating of geochronology within a range of 80 Myr (Nichols Jr et al., 1994; Fehn et al., 2000).

In environmental sciences, $^{129}$I can be used to study the biogeochemical cycle of stable iodine (Santschi and Schwehr, 2004; Snyder and Fehn, 2004; Schwehr et al., 2005; Karcher et al.). Duo to high releases from nuclear acci-
dent, $^{131}$I is one of the most important and harmful radionuclides to the human health. However, it soon becomes undetectable in the environment due to its short half-life ($T_{1/2} = 8$ days). Therefore $^{129}$I can help to reconstruct $^{131}$I dose in order to evaluate $^{131}$I deposition patterns after nuclear accidents (Schmidt et al., 1998; Michel et al., 2005). It is also an important radionuclide to assess the safety of radioactive waste repositories.

In view of the highly soluble and mobile nature of iodine, $^{129}$I could be used as a good tracer in hydrogeological studies. Applications in this field include the tracking of surface water movement processes from infiltration to subsurface flow, investigating the sources and migration characteristics of groundwater, assessment of interactions between surface water and groundwater, as well as estimating age and residence time of groundwater in recharge areas (Fabryka-Martin et al., 1985; Fabryka-Martin et al., 1987; Lehmann et al., 1993; Moran et al., 1998). The sample volume needed for $^{129}$I analysis is relatively small and the isotope often has a greater magnitude of anthropogenic signal than any other traditional tracers (e.g. $^{137}$Cs, $^3$H) in hydrological research (Santschi et al.).

As a highly conservative tracer that maintains a strong and consecutive signal in seawaters, $^{129}$I became a potential tracer in oceanography. Variations of $^{129}$I concentration and $^{129}$I/$^{127}$I ratio in oceans clearly reflect movement and pathways of currents, circulation, mixing and exchanges of water masses, as well as the transport and diffusion patterns of anthropogenic pollutants (Karcher et al., 1998; Smith et al., 1999; Hou et al., 2007; Schnabel et al., 2007; Orre et al., 2010). Time series analysis of $^{129}$I/$^{127}$I and comparison of available release functions from specific NRFs, the early discharge records could be established (Raisbeck et al., 1995; Raisbeck and Yiou, 1999; Gallagher et al., 2005; Reithmeier et al., 2006). In addition to being a retrospective tracer, $^{129}$I can also be applied to obtain information of transit time and transfer factor (TF) of contaminants (Smith et al., 1998; Raisbeck and Yiou, 1999; Smith et al., 1999; Hou et al., 2000a; Smith et al., 2005; Keogh et al., 2007; Smith et al., 2011).

Speciation analysis of $^{129}$I provides a powerful tool for gaining a detailed picture of sources and exchange of water masses in the ocean compared to using total $^{129}$I alone. Moreover, speciation of both isotopes offers additional information by identifying redox rates of I/IO$_3^-$ pairs in environmental conditions. The huge discrepancy between iodide/iodate for $^{127}$I and $^{129}$I reflects different sources of iodine isotopes. These potentials have been successfully applied in the North Sea and the Baltic Sea (Hou et al., 2001; Hou et al., 2007; Hansen et al., 2011b; Yi et al., 2012). Because iodine exhibits different behaviors (i.e. mobility and bioavailability) in terms of species in the environment, speciation of $^{129}$I in soil, atmosphere and biological samples is therefore helpful in understanding the stable iodine ($^{127}$I) cycle. However, determination of the individual species of $^{129}$I is difficult and thus speciation analysis of $^{129}$I is mainly focused on the determination of different $^{129}$I-
bounded fractions in these samples (Wershofen and Aumann, 1989; Hou et al., 2000c; Hou et al., 2003).

Continuous release of $^{129}$I from NRFs and the tremendous amount of it (up to 70 tons) that is waiting for reprocessing makes $^{129}$I a source of potential environmental hazard in the long run. Therefore, it is important to monitor the levels of $^{129}$I in order to evaluate and predict the consequences for both the environment and humans, since $^{129}$I is taken up by organisms and eventually enters the food chain.
2. A short review of iodine ($^{127}$I and $^{129}$I) and its species in natural surface environments

2.1 $^{127}$I and $^{129}$I in fresh water (rivers and lakes)

Concentrations of $^{127}$I in rivers and lakes are not fully investigated and the available data are scarce, scattered and vary widely (0.01-73 ppb, commonly at a range of 0.1-20 ppb) (Fuge and Johnson, 1986; Moran et al., 2002a). As the main contributor of iodine is expected to be rainfall, concentration of $^{127}$I in non-marine surface waters varies with respect to its locations and local soil types, with a mean value of 5 ppb. Oceanic iodine is delivered to lakes and rivers through dry/wet deposition and sea-spray. This branch of the iodine cycle tends to lift iodine level in its surrounding fresh water system. Another source is land-derived, by weathering of soils and rocks (Oktay et al., 2001). Surface waters with high content of iodine were also reported in drainage from industrialized and urban rather than rural areas (Whitehead, 1979). Other sources such as vegetation volatilization, degradation of organic matter and groundwater disturbance are, however, regarded as minor fractions (Moran et al., 2002b). Iodide and dissolved organic iodine (DOI) are the predominant species in surface fresh waters with generally high iodide concentration in estuaries (Smith and Butler, 1979; Oktay et al., 2001; Schwehr and Santschi, 2003). However, high iodate was reported in some lake waters, which contradict traditional points of view (Jones and Truesdale, 1984). Interconversion between iodine species is suggested to be driven by biological activities in lakes, but this redox process is not pronounced when compared to some marine waters (Jones and Truesdale, 1984).

Variation of $^{129}$I in surface fresh water is even larger than that of $^{127}$I, with the concentrations of $^{129}$I spanning from $10^6$ to $10^{10}$ atoms/L and $^{129}$I/$^{127}$I ranges between $10^{-11}$ and $10^{-5}$ (Snyder et al., 2010). However, the concentration of $^{129}$I can be even lower than $10^6$ atoms/L in areas remote from the anthropogenic effects. High $^{129}$I concentrations appeared in fresh water systems of Europe and North America with a typical range of $10^8$-$10^9$ atoms/L ($10^{-7}$-$10^{-5}$ for $^{129}$I/$^{127}$I), suggesting that the influence of NRFs is already evident in continental surface water bodies (Beasley et al., 1997; Rao and Fehn, 1999; Cochran et al., 2000; Buraglio et al., 2001b; Moran et al., 2002a; Keogh et al., 2010). Since a huge amount of $^{129}$I has been introduced into the marine system, oceanic re-emission of $^{129}$I could be another important source
in terrestrial waters. Positive correlations were found for $^{129}\text{I}/^{127}\text{I}$ in lake waters (collected in the English Lake District) as a function of distance from Sellafield/Irish Sea, which implied a strong influence by both Sellafield and the Irish Sea (Atarashi-Andoh et al., 2007). Rapid temporal variation of $^{129}\text{I}$ in English and Irish rivers was a response to the change of gaseous release from Sellafield NRF, while this change was not pronounced in rivers far distant from NRFs, such as in Sweden (Buraglio et al., 2001b). Nevertheless, atmospherically transported $^{129}\text{I}$ from Sellafield NRF was also regarded as a major source of $^{129}\text{I}$ in Swedish lakes, where concentrations of $^{129}\text{I}$ was up to $1.4 \times 10^9$ atoms/L and a strong latitudinal dependence was observed (Kekli et al., 2003). Contribution of $^{129}\text{I}$ from the Chernobyl accident seems to be insignificant in relation to elevated $^{129}\text{I}$ level in European lakes, even for those located in the areas of high Chernobyl fallout (Buraglio et al., 2001a). Similarly, local power plants are also believed to have limited influences (Rao and Fehn, 1999; Hou et al., 2002). Considering the fact that iodine easily attaches to suspended particles or binds to organic materials, regional properties such as watershed characteristics (e.g. river flow rate, evapotranspiration rate, catchment areas and vegetation coverage, etc.) and intensity of agricultural and other anthropogenic activities may be involved in altering the $^{129}\text{I}/^{127}\text{I}$ in rivers (Oktay et al., 2001; Moran et al., 2002b; Kekli et al., 2003), which can be used to trace organic carbon in estuarine waters (Schwehr et al., 2005).

Compared to the dramatic $^{129}\text{I}$ value of $\sim 10^{10}$ atoms/L found in the Savannah River (USA; Moran et al., 2002a), the $^{129}\text{I}$ levels in surface waters of the southern hemisphere, which is far from the point sources, are 2-4 orders of magnitude lower ($10^6-10^8$ atoms/L, $^{129}\text{I}/^{127}\text{I} > 10^{-11}$) (Snyder and Fehn, 2004), indicating spread of anthropogenic $^{129}\text{I}$ on a global scale, even in remote Antarctica. This anthropogenic $^{129}\text{I}$ in the southern hemisphere includes not only bomb fallout, but also NRF signals from the northern hemisphere. It seems that, however, the distribution of $^{129}\text{I}$ in rivers and lakes is not uniform, but latitudinal-dependent (Fehn and Snyder, 2000). Higher levels of $^{129}\text{I}/^{127}\text{I}$ in middle latitude of both hemispheres compared to equatorial and polar regions are probably associated with atmospheric circulation coupled with precipitation patterns on a global scale. Local ecology and marine productivity are also important factors that affect the terrestrial distribution of $^{129}\text{I}/^{127}\text{I}$ worldwide.

2.2 $^{127}\text{I}$ and $^{129}\text{I}$ in seaweed

Iodine can be concentrated in seaweeds with a concentration factor (CF) as high as $10^6$ in some species (Hou et al., 1997), and thus is an ideal bioindicator that is sensitive to its surrounding environment. Concentration of iodine in seaweeds is often higher than inland plants ($< 10^6 \text{ g} \cdot \text{g}^{-1}$)
(Rucklidge et al., 1994). This feature might indicate that seaweeds are more efficient in building up iodine than terrestrial plants, or can be related to difference of iodine speciation between land surface and seawaters. Iodine concentration in seaweeds varies remarkably ($10^{-5}$-$10^{-3}$ g·g$^{-1}$ (dry weight)) and it is reported to be species- and seasonal-dependent, but normally at the level of $10^{-4}$ g·g$^{-1}$ (dry weight) (Hou et al., 1997; Hou and Yan, 1998; Osterc and Stibilj, 2008). Similarly, iodine speciation in marine algae shows a tremendous difference in relation to species of algae. More than 99% of iodine in brown algae is water-soluble, while in some green algae it is < 10%. Further, > 60% and < 40% is iodide and organic iodine in the aqueous leachate, respectively, and the iodate is the least component (< 5%) (Hou et al., 1997). The iodine of water-insoluble form, is mainly bounded with protein, and a lesser content with pigment and polyphenol (Hou et al., 2000c). This chemical speciation of iodine in seaweeds is important as it is linked to bioavailability and biological toxicity.

It is suggested that comparable iodine isotopes ($^{129}$I and $^{127}$I) are taken up and assimilated by algae. Therefore $^{129}$I/$^{127}$I in seaweed is usually used as a biological indicator that reflects local level of $^{129}$I in seawaters. Additionally, $^{129}$I/$^{127}$I in combination with $^{129}$I/$^{137}$Cs and $^{129}$I/$^{99}$Tc are commonly applied to trace the geochemical cycle of $^{129}$I temporally and spatially (Cooper et al., 1998; Hou et al., 2000a; Nies et al., 2010). Because of the sensitive response of $^{129}$I level in seaweed to $^{129}$I release from NRFs, time series of $^{129}$I in seaweeds samples were successfully applied as an oceanographic tracer to reconstruct the missing release record of NRFs in early stages of operation. Furthermore, this approach was coupled with investigations of the ocean current circulation and estimate of transit times, as well as the initial $^{129}$I/$^{127}$I ratio prior to anthropogenic nuclear activities (Raisbeck et al., 1995; Kershaw et al., 1999; Raisbeck and Yiou, 1999; Yiou et al., 2002; Fehn et al., 2007; Keogh et al., 2007; Hou et al., 2009a).

$^{129}$I concentration in seaweeds varies from $10^{8}$ to $10^{12}$ atoms/g (dry weight) and depends on species and sampling locations, while $^{129}$I/$^{127}$I in marine algae has increased by 3-4 orders of magnitude from $\sim 10^{-10}$ to $10^{-6}$ in the last two decades. This increase is mainly due to the increase of $^{129}$I discharges from NRFs since the 1990s. The highest levels were of course found in the coastal waters of the Irish Sea and the English Channel, where the $^{129}$I/$^{127}$I in seaweed was $> 10^{5}$ (Raisbeck et al., 1995; Frechou and Calmet, 2003; Keogh et al., 2007). Other relatively high levels ($10^{8}$-$10^{7}$) were reported from Denmark and the Norwegian coast, which are apparently contaminated by $^{129}$I plumes from the Sellafield and La Hague advected water towards the north (Hou et al., 2000a; Yiou et al., 2002). In areas remote from the NRFs, which are less or indirectly influenced by $^{129}$I-contaminated marine currents, the $^{129}$I/$^{127}$I in seaweeds is in the order of $10^{-9}$ (Hou et al., 2000a; Keogh et al., 2007; Osterc and Stibilj, 2008). Extremely low $^{129}$I/$^{127}$I levels of $10^{-16}$ or less were measured in Japan, China and USA, as well as the Beaufort and Bering
Seas in the Arctic Ocean. These regions are believed to be less affected by releases from Sellafield and La Hague thus the $^{129I}/^{127I}$ in seaweeds are therefore close to the global fallout level (Kilius et al., 1994; Tseng and Chao, 1996; Cooper et al., 1998; Hou et al., 2000b).

2.3 $^{127I}$ and $^{129I}$ in the atmosphere and precipitation

In the atmosphere, iodine exists as particle/aerosol associated, inorganic gaseous (e.g. $\text{I}_2$, HI, HIO, etc.) and organic gaseous (CH$_3$I, CH$_2$I$_2$, etc) substances. Low concentrations of $^{129I}$ were found in the atmosphere with an order of $10^4$-$10^5$ atoms/m$^3$ ($10^{-8}$-$10^{-9}$ for $^{129I}/^{127I}$ ratio) (Santos et al., 2005). The long time needed for $^{129I}$ and $^{127I}$ to approach their equilibrium combined with the long time needed to approach their isotopic equilibrium, suggest a different distribution of $^{129I}$ and $^{127I}$ speciation in atmosphere (Wershofen and Aumann, 1989). In general, for both $^{129I}$ and $^{127I}$, gaseous organic iodine is the predominant form in the atmosphere, followed by the gaseous inorganic form, while the particle associated iodine content comprises normally < 20% (Wershofen and Aumann, 1989; Hou et al., 2009b; Michel et al., 2012). Furthermore, for $^{129I}$, the closer to the NRFs, the higher the content of the gaseous organic form, which is not observed for $^{127I}$ (Hou et al., 2009b) and photochemical processes were suggested to change the chemical forms of atmospheric iodine. $^{129I}/^{127I}$ values in all iodine species were at a similar level (~ $10^{-7}$). Differently, the highest $^{129I}/^{127I}$ was measured in particle associated form, and in organic and inorganic gaseous forms, $^{129I}/^{127I}$ were 3.1 and 1.2×$10^{-7}$, respectively (Michel et al., 2012). Particle associated iodine is suggested to play a role in cloud formation. High IO$_3$/I$^-$ was found in oceanic-derived aerosols (1.5-3.0), which was attributed to the accumulation of iodate, as well as to the depletion of iodide depending on aerosol pH ($\text{I}^- + \text{HIO} + \text{H}^+ = \text{IX}^\dagger + \text{H}_2\text{O}$) (Vogt et al., 1999; Baker, 2004). However, the rate of this reaction, as well as the formation of iodate was suggested to be slow since a significant proportion of iodide was observed in precipitation (Baker et al., 2001).

Available data on concentration of $^{129I}$ in precipitation varies temporally and spatially (~ $10^7$-$10^{10}$ atoms/L) while $^{127I}$ is normally around 1-2 μg/L. In rainwater, iodide is the major specie for $^{129I}$ while $^{127I}$ mainly exists as iodate (Hou et al., 2009a; Lehto et al., 2012). In general, concentrations of $^{129I}$ in rain waters were observed to be higher in coastal areas compared to inland, and are strongly determined by whether the air masses have passed the NRFs areas before precipitation (Bachhuber and Bunzl, 1992; Aldahan et al., 2009; Keogh et al., 2010). In addition, it seems that the concentration of $^{129I}$ could be continuously lowered by washing out during a rainfall event (López-Gutiérrez et al., 2001; López-Gutiérrez et al., 2004). Extremely high $^{129I}$ concentrations of > $10^{10}$ atoms/L were found in Germany and Ireland, im-
plying a significant influence by atmospheric release of $^{129}$I from NRFs, nuclear accidents, as well as the influence from highly $^{129}$I-contaminated ocean water (Paul et al., 1987; Krupp and Aumann, 1999b; Keogh et al., 2010). It is suggested that, re-emission of $^{129}$I from the ocean surface is the major source that contributed to $^{129}$I of rainwater in the European continental coast areas (Hou et al., 2009a).

In most areas of Europe, $^{129}$I in precipitation is in the order of $10^8$-$10^9$ atoms/L (~ $10^{-7}$ for $^{129}$I/$^{129}$I) without any specific correlation to latitude (Buraglio et al., 2001b; Persson et al., 2007; Reithmeier et al., 2005), implying a large coverage of NRFs influences. Moreover, $^{129}$I released into the atmosphere from NRFs has enough time to travel over long distances based on a suggested residence time of 10-18 days in the atmosphere (Duce et al., 1963), and thus provides a significant source of $^{129}$I in regions far away from those directly influenced by Sellafield and La Hague. Rainwater samples collected from USA demonstrate the possible influence from Europe, although the concentrations were 1-2 orders of magnitude lower (Oliver et al., 1982; Moran et al., 1999; Rao and Fehn, 1999).

### 2.4 $^{127}$I and $^{129}$I in soil and sediment

Iodine in soil mainly originates from the sea after wet/dry deposition of atmospheric iodine, or by weathering of rocks. Concentrations of iodine in soils are suggested to decrease with increasing distance from the coast, although some controversies about this issue exist (Fuge and Johnson, 1986; Moran et al., 2002a). Iodine concentration in European surface soil varies at 1-10 μg·g$^{-1}$ which is affected by rock/soil types, hydrological conditions and land use practices. Eh/pH conditions may play a major role in iodine distribution since iodide tend to volatilize in acid soils, while iodate is more stable in alkaline soils (Rucklidge et al., 1994).

Soil is the largest $^{129}$I reservoir of the terrestrial environment. Most $^{127}$I resides in the top 0-50 cm depth, and $^{129}$I is primarily retained within the upper 10 cm at the order of $10^7$-$10^{10}$ atoms/g ($10^9$-$10^{10}$ for $^{129}$I/$^{129}$I) in Europe (Ernst et al., 2003; Michel et al., 2005; Hansen et al., 2011). Because of the injection of anthropogenic $^{129}$I from major NRFs, surface soils in most adjacent areas are contaminated (Muramatsu and Ohmomo, 1986; Rao and Fehn, 1999). High levels of $^{129}$I were observed in many samples of European soil which is influenced by Sellafield and La Hague. Besides, sources of Chernobyl fallout is evident in surface soils collected from Ukraine, Belarus and Russia (Hou et al., 2003; Michel et al., 2005). Soil depth profiles show different depth dependencies of the $^{127}$I and $^{129}$I concentrations and exponential decrease was observed for both isotopes, though the slope of $^{129}$I was much steeper in upper 25 cm (Ernst et al., 2003).
$^{127}$I in the top part of sediments is generally 5-10 times higher than that in soils ($> 10 \, \mu g \cdot g^{-1}$) (Englund et al., 2008; Hansen et al., 2011; Osterc and Stibilj, 2012; Qiao et al., 2012). $^{129}I/^{127}I$ in lake sediments and marine sediments varies considerably and can provide a time marker for $^{129}I$ emissions and depositions (Moran et al., 1998; Gallagher et al., 2005). Inventories of iodine in sediments varies a lot depending on sorption coefficients, dynamic sedimentation and erosion processes (Snyder et al., 2010). In many $^{129}I$-contaminated seas, accumulated $^{129}I$ was found in the top 5-10 cm of marine sediments in the range of $10^9$-$10^{11}$ atoms/g (Wilkins, 1989; López-Gutiérrez et al., 2004a; Aldahan et al., 2007b). However, in marine sediments collected off the USA coast that are remote from European NRFs, the $^{129}I/^{127}I$ is in good agreement with the pre-nuclear era natural level (Fehn, 1986; Moran et al., 1998).

Sequential extraction is widely used in fractionation analysis of iodine in soil and sediment samples and a similar distribution of $^{129}I$ in soil and sediment is observed (Hou et al., 2003). Generally, around 80% of $^{129}I$ is bound to oxides and organic matter, and less than 10% of soil leachate are water soluble and exchangeable fractions (Hou et al., 2003; Hansen et al., 2011; Qiao et al., 2012). An exception was reported in soil collected in Germany, where ~ 50% of readily available $^{129}I$ form was observed, which was attributed to specific soil properties and chemical speciation of deposited $^{129}I$ (Schmitz and Aumann, 1995). In the organic fraction, $^{129}I$ was mainly associated with humic and fulvic acids. In addition, it is suggested that the anoxic/oxic conditions may influence the mobility of soil iodine (Hansen et al., 2011) as well as the iodine speciation in the water soluble fraction (Yuita, 1992). For $^{127}I$, though the major fraction is bound to oxides and organic matter, the composition is different when compared with $^{129}I$ because a significant fraction of $^{127}I$ is not extractable.

2.5 $^{127}I$ and $^{129}I$ in oceans

The ocean is the major iodine reservoir and concentration of $^{127}I$ in seawater is generally rather uniform (~ 60 ppb). The initial natural ratio of $^{129}I/^{127}I$ introduced into the ocean is estimated to be $1.5 \times 10^{-12}$ without spatial difference, in theory, due to much longer residence time of iodine (30,000 yr) than seawater turnover time (1000 yr) (Broecker and Peng, 1982; Fehn et al., 2007). However, because of human nuclear activities since the 1940s, more than 6000 kg of $^{129}I$ have been introduced into the environment, leading to dramatic increase of $^{129}I$ in the world oceans. Nuclear fuel reprocessing is regarded as the major anthropogenic iodine contributor and releases from those facilities dominate the $^{129}I$ inventory nowadays. Sellafield (UK) and La Hague (France) are the main point sources of $^{129}I$, and together they account for 90% of total global emissions. The temporal and spatial variability of
anthropogenic $^{129}$I is strongly linked to the major point sources in the Irish Sea and the English Channel and the global marine spreading pathways are partly outlined from these sources. However, most of the available $^{129}$I data are assembled from small territories and there is no comprehensive picture about the magnitude of $^{129}$I distribution in different parts of the world oceans or with respect to water depth (Schink et al., 1995; Carmack et al., 1997; Beasley et al., 1998; Buraglio et al., 1999; Cooper et al., 2001; Smith et al., 2005; Suzuki et al., 2008; He et al., 2010; Povinec et al., 2010). A review of the $^{129}$I variability in the world oceans is compiled in paper I of this thesis and is presented in section 4.1.
3. Sampling sites and analytical techniques

3.1 Sampling sites

3.1.1 2010/2011 Southern Ocean expedition

The 2010/2011 Antarctica two-ship expedition was an international scientific cruise jointly funded by the Swedish Polar Research Secretariat and the US National Science Foundation (NSF). This Antarctica scientific expedition was devoted to studies of physical and chemical oceanography, sea ice, the carbon cycle, the dynamics of Amundsen Sea Polynya, and ecosystems. Investigation of iodine was one of the expedition’s projects and was conducted through a joint cooperation between the Uppsala group (Department of Earth Sciences and The Tandem Laboratory) and the Danish group at the Center for Nuclear Technologies, Technical University of Denmark, Risø Campus. The aims of the project are focused on the distribution of the iodine isotopes ($^{129}$I and $^{127}$I) and species of iodine (I$^-$ and IO$_3^-$) along the expedition transect. During October-December 2010, the Swedish icebreaker Oden sailed from Landskrona (Sweden) to Punta Arenas (Chile) via the North Sea, the English Channel and the Atlantic Ocean (Figure 3.1). Surface water samples along the first transect of the expedition (North Sea - Canary Islands) represent the material for this thesis.

Surface water samples were continuously collected through the Teflon pipes at the Oden water lab. The water samples were planned for analysis of tracer elements, such as iodine, uranium and cesium. Meanwhile, other sampling devices (i.e. Denuder sampler, PM 2.5 sampler, etc.) were set up onboard to collect air samples along the cruise from Sweden to South America, which were aimed for the investigation on organic and inorganic halogen species in the marine boundary layer (MBL). Further, a standard CTD sampler was launched to automatically measure water temperature and salinity along the transect. Meteorological parameters such as wind velocity and humidity were also measured at the same time.

Atlantic surface water was continuously sampled at varying sampling density and volume depending on location and expected $^{129}$I concentration. Sampling strategy along the Oden route from north to south (Figure 3.1) varied depending on expected variability of $^{129}$I concentration in the different water bodies. In addition, the volume of water samples was gradually in-
creased from 0.5 L to 2.0 L along the transect in response to the expected $^{129}$I concentration in the water.

Figure 3.1: Atlantic transect of icebreaker Oden from Sweden to Chile. Different colors represent different strategies of surface seawater sampling. Sampling at each 5 km with 0.5 L for each seawater sample was implemented within the English Channel (purple). Sampling at each 20 km was performed in the North Sea (red, 1.0 L each sample) and each 50 km in the Celtic Sea and the northeastern Atlantic Ocean (yellow, 2.0 L each sample), while 100 km a part sampling was carried out in the rest of the transect (green, 2.0 L each sample).

3.1.2 The North Sea samples

The North Sea is a semi-enclosed shallow continental shelf sea with an average of water depth 90 m and lies between 51°N and 62°N where prevailing westerlies dominant. It connects to the saline Atlantic Ocean through Orkney-Shetland-Norwegian channels in the north and the English Channel in the southwest, while it exchanges with brackish Baltic water via the Danish straits. General cyclonic circulation within the North Sea relates to its strong tidal currents and southwesterly wind, and is modified by specific topography and bathymetry (Howarth and Oceanographic, 2001).

In its southern part and the coastal areas of the German Bight where the water is well mixed throughout the year, the depth is less than 40 m. Depth
in the central and north parts gradually increases from 40 m to 200 m, while in the Norwegian Trench, northeast, deeper regions occur with the deepest, about 750 m, in the Skagerrak. Therefore in these regions, the water column usually stratifies in May with a mean thermocline of 30 m, in particular in the Norwegian Trench (Richardson and Pedersen, 1998; Howarth, 2001). Due to the relatively high $^{129}$I level in the North Sea, only 0.5 L surface seawater was collected at each sampling site for $^{129}$I separation and analysis.

3.1.3 English Channel and Celtic Sea samples
The English Channel is a narrow shallow passage that separates southern England from the European continent. It connects to the Atlantic Ocean in the west and the North Sea through the Dover Strait in its eastern end. The width of the English Channel narrows gradually from the west to east, while the average depth decreases from 120 m to 45 m. The Celtic Sea is an extension of the European continental shelf that opens to the deep Atlantic Ocean. Its northern and eastern limits are bound by the southern Irish Sea and the English Channel, respectively, while the western and southern parts are bordered by the continental slope. The water is relatively shallow (< 100 m) in its northern portion and increases towards south and west with the longest open boundary normally defined by the 200 m isobathymetry.

Saline Atlantic water partly enters the English Channel north of Ushant Island (France) and flows eastwards within the channel. Accordingly, an evident gyre is isolated from the main flow in the Gulf of Saint Malo (Salomon and Breton, 1993). Another fraction of Atlantic water moves north along the coast from the Isles of Scilly to Lundy Island in the Celtic Sea and returns southwestward through the St. George’s Channel. This flow pattern continues along the Irish coast thus a counterclockwise current is suggested (Brown et al., 2003). In addition, a weak residual current flows poleward along the west continental slope (Southward et al., 2005). The currents in the Celtic Sea mainly respond to the variation of wind systems in this region, where in summer the westerly winds dominate while wind direction is more southwesterly in winter (Pingree and Le Cann, 1989).

It is expected that large variations in $^{129}$I concentration occur between the east and west parts of the English Channel. Therefore frequent sampling density was applied within the English Channel, in all 34 samples of 0.5 L each. A small number of samples, only six, were collected in the Celtic Sea, with a volume of 1.0 liter each.

3.1.4 The northeastern Atlantic Ocean samples
Although in general the surface ocean waters flow eastward, the whole region of the northeastern Atlantic Ocean is considered to be stagnant (Pingree, 1993). This region is located between subpolar and subtropical gyres where
seasonal and regional variations of wind systems in this transition zone (between westerlies and trade winds) highly influence the surface circulation pattern in most parts of the sampling transect. A branch of the North Atlantic Current (NAC) borders the transect in the north, while the southern limit is influenced by a combination of the Azores, Portugal and Canary Currents systems, as well as the injection of Mediterranean Outflow Water (MOW) (Figure 3.2).

Figure 3.2: General bathymetric chart of the investigated area in the northeastern Atlantic Ocean. (a) Sampling transect of $^{129}$I along the northeastern Atlantic Ocean. Sampling locations are expressed as black dots. Location of Sellafield and La Hague nuclear reprocessing facilities (NRFs) is highlighted with stars. (b) General scheme of surface water circulation in the Bay of Biscay and (c) the Gulf of Cadiz. NAC=North Atlantic Current, IPC=Iberian Poleward Current, PC=Portuguese Current, $AC_N$=Azores Current, northern branch, $AC_S$=Azores Current, southern branch and CC=Canary Current.

Intensive in situ hydrographic data and sea surface temperature (SST) satellite observations, as well as numerical models reveal that the eastward Azores Current, combined with the equatorial Portuguese Current that flows parallel to the west Iberia coast, enters the Gulf of Cadiz along the continental slope towards the Strait of Gibraltar. The easternmost part of this anticyclonic circulation eventually feeds the Canary Current. This general fea-
ture of circulation pattern is thought to be weakened in winter and enhanced in summer (Johnson and Stevens, 2000; Relvas and Barton, 2002; Sánchez and Relvas, 2003).

Saline and dense MOW mixed with overlying North Atlantic Central Water (NACW) descends as the Mediterranean Undercurrent in the Gulf of Cadiz along the continental slope and interacts with bottom topography. High velocity Mediterranean Water arising from the release of potential energy makes this region highly unstable (Baringer and Price, 1999). On its way to Cape St. Vincent, the plume becomes neutrally buoyant and divides into two parts with their main cores lie at 800 m and 1200 m depth (Zenk, 1970). These Mediterranean waters can be traced across the North Atlantic Ocean along 40°N and even extend to the south of the Iceland-Scotland Ridge (Reid, 1978). Ambar (Ambar, 1983) also identified a shallow Mediterranean core of 400-700 m depth, stretching from the vicinity of the Strait of Gibraltar to the area off the Cape Roca of the western Portugal coast. Mauritzen et al. (Mauritzen et al., 2001) make a point that a salinity detrainment process (towards low-density levels fluxes) occurs in the eastern Gulf of Cadiz, which partly results in a higher salinity of East North Atlantic Central Water compared to that in the west.

Many models and direct observations show that the Atlantic Water not only flows eastward towards the Mediterranean Sea, but also has a recirculation within the upper layers in the Gulf of Cadiz (Johnson and Stevens, 2000; Mauritzen et al., 2001; Machín et al., 2006) (Figure 3.2). During winter, an Iberian Poleward Current was observed along the Portugal coast as a recirculation of the Azores Current (AC) which centered at about 35°N (Mazé et al., 1997; Peliz et al., 2005). Although the origin and variability of this slope-flow current is still unclear, it may be connected with the coastal counter flow in the western Cadiz. The main route of this westward flowing Atlantic Water is along the slope of the European continent and it is well defined west of Cape Santa Maria and strengthened around Cape St. Vincent. Thus the modified surface water in the Gulf of Cadiz can subsequently spread westward and northward.

Considering long-term currents circulation patterns in the northeastern Atlantic Ocean, as well as the relatively long distance from Sellafield and La Hague, concentration of $^{129}$I should be low in this region (31.07-47.36 °N, 7.96-14.52°W). Therefore, the sampling frequency was reduced and the volume of each sample was increased to 2 liters.
3.2 Measurement technique of iodine (\(^{127}\)I and \(^{129}\)I) from seawater

3.2.1 Sample preparation and chemical reagents

All collected samples were instantly filtered onboard through a 0.45 \(\mu\)m membrane (Sartorius AG, Gottingen, Germany) and filled in clean polyethylene containers under cold and dark conditions. \(^{129}\)I standard (NIST-SRM-4949c) was purchased from National Institute of Standard and Technology (Gaithersburg, MD, USA). Carrier-free \(^{125}\)I was purchased from Amersham Pharmacia Biotech (Little Chalfout, Buckinghamshire, UK) and carrier \(^{127}\)I (Woodward iodine) from MICAL Specialty Chemicals (New Jersey, USA). Bio-Rad AG1- \(\times 4\) anion exchange resin (50-100 mesh, Cl\(^-\) form, Bio-Rad laboratories, Richmond, CA) was used for iodine separation because of different affinities of iodide and iodate on the resin. All chemical reagents used were of analytical grade and all solutions were prepared using deionised water (18.2 M\(\Omega\) cm\(^{-1}\)).

A large column was loaded with AG1- \(\times 4\) anion exchange resin (50-100 mesh, in Cl\(^-\) form) and washed with 300 ml of 2 mol/L NaNO\(_3\) until Cl\(^-\) ion was washed off from the resin. Afterwards the column was washed with 50 ml deionised water. Then the prepared converted resin (in NO\(_3\)\(^-\) form) was transferred to a column (\(\Phi\) 1.0 \(\times\) 20 cm) for separation of iodine.

3.2.2 Separation of iodide and iodate from seawater

A method for separation of iodine species (iodate and iodide) developed by Hou et al. (Hou et al., 2001) was used in the experiment (Figure 3.3). The filtered seawater, mixed with 0.1 ml of \(^{125}\)I tracer (250 Bq), was loaded to the prepared AG1- \(\times 4\) NO\(_3\)\(^-\) form column (\(\Phi\) 1.0 \(\times\) 20 cm) with a flow rate 2-4 ml/min. After the seawater pass through, the column was washed with 30 ml deionised water and followed by 50 ml of 0.2 mol/L NaNO\(_3\). The effluent was collected for solvent extraction of iodate. The iodide (including \(^{125}\)I), however, is adsorbed onto the resin, and can be eluate with 60 ml of 10% NaClO solution. The eluate is used for iodide extraction. Meanwhile, 1.0 ml of the effluent seawater, as well as the eluate was used for determination of \(^{127}\)I using ICP-MS (Inductively Coupled Plasma Mass Spectrometry).

3.2.3 Extraction of iodine species (\(^{127}\)I and \(^{129}\)I)

To extract iodate and total inorganic iodine, 1.0 ml of \(^{127}\)I carrier (Woodward iodine, 2 mg/ml) and 0.1 ml tracer (\(^{125}\)I, 250 Bq) were added to the filtered seawater and the effluent of the iodate fraction. In order to reduce all the iodine to iodide form, 10 ml 3 mol/L HNO\(_3\) and 1.0 ml of 1 mol/L Na\(_2\)S\(_2\)O\(_5\) were added in turn, and the pH was maintained at < 2 to ensure a fast reduc-
tion. Then the mixed solution was transferred to a suitable separation funnel with addition of 20-50 ml CHCl₃. Iodide was oxidized to iodine (as I₂) by using 2-5 ml of 1.0 mol/L NaNO₂ and extracted to the CHCl₃ phase. This procedure is repeated two times to extract all iodine to organic phase. 0.5 ml of 3 mol/L HNO₃ is added to the funnel to provide enough hydrogen ions before oxidizing iodide in each extraction. The extraction of iodate from the eluate is much the same. The differences are that we use a 1.0 mol/L NH₂OHHCl solution to reduce iodate to molecular iodine. Finally, 0.2 ml of 0.05 mol/L Na₂S₂O₅ was added to the funnel and iodine in the organic phase was back-extracted to the water phase, then transferred to a vial to which 0.1 ml of NH₃·H₂O was added to remain iodide stable before precipitation. The precipitation of AgI was achieved through addition of 1.0 mol/L AgNO₃. The AgI precipitate was dried at 70°C.

**Figure 3.3:** Analytical scheme for chemical speciation of ¹²⁷I and ¹²⁹I species from seawater. Modified from (Hou et al., 2001).

The chemical separation yield is obtained by measurement of ¹²⁵I in the final separated solution and the ¹²⁵I added to the solution (as standard) using a NaI
gamma detector (well type, Bicron) at channels 25-115 in 26-36 keV for 60 seconds. The chemical yield (Y) is calculated by: \( Y = \frac{\text{counts of sample}}{\text{counts of } ^{125}\text{I standard}} \). The chemical yield of total iodine, iodate and iodide during the separation processes were calculated to be 81-99%, 97-99% and 53-80%, respectively.

3.2.4 ICP-MS determination of \(^{127}\text{I}\)
Measurement of \(^{127}\text{I}\) was performed using X-Series inductively coupled plasma mass spectrometry (ICP-MS) system under hot plasma conditions with Xt interface. Before measurements, each 1.0 mL of raw sample was spiked with \( \text{Cs}^+ \) as internal standard, and then diluted to 20 mL with 1% of ammonium solution. The detection limit for \(^{127}\text{I}\) calculated as 3 SD of blanks was 0.05 ng/mL.

3.2.5 AMS determination of \(^{129}\text{I}\)
The dried silver iodide precipitation (AgI) was mixed with niobium powder (~7.4 mg) in a mass ratio of 1:2. The mixed sample was then transferred and pressed into a copper holder for the AMS measurement in the Tandem Laboratory, Uppsala University. Negative ions beam of iodine is sputtered out from the copper holder and selected by a 90° bouncer magnet. A voltage of 3.5 MV was applied in the terminal to measure \(^{129}\text{I}\). The \(^{129}\text{I} /^{127}\text{I}\) isotopic ratio in the standard (NIST-SRM-4949C) is \((1.1\pm0.1) \times 10^{-11}\) and the ultra-low background of the AMS system is \(4\times10^{-14}\). The statistical error of the measurements was < 10% (one standard deviation).
4. Results and discussion

The whole data sets of $^{129}\text{I}$ and $^{127}\text{I}$ and their species along the transect are shown in Figure 4.1 and 4.2. Because of the huge number of data and the large variability in oceanographic characteristics of the transect areas, the data were divided into four sets representing the regions: the North Sea (NS, paper II), the English Channel (EC, paper III), the Celtic Sea (CS, paper IV) and the northeastern Atlantic Ocean (NEAO, paper V). Detailed discussion of each region is given in this section. Furthermore, a review of $^{129}\text{I}$ distribution in the marine waters is given in paper I and summarized in section 4.1.

*Figure 4.1:* Analytic results of $^{129}\text{I}$ and its species along the transect of *Oden* Antarctica expedition used in this thesis. NS = North Sea, EC = English Channel, CS = Celtic Sea, NEAO = northeastern Atlantic Ocean.
4.1 Distribution of $^{129}$I in global oceans

The $^{129}$I concentration spans from $6.0 \times 10^6$ atoms/L (southern Indian Ocean) to $1.3 \times 10^{12}$ atoms/L (Irish Sea) which is 1.3-6 orders of magnitude compared to pre-anthropogenic background value. The Nordic Seas and the Arctic Ocean present the major $^{129}$I reservoir, while the Pacific and Indian Oceans have low concentrations close to the nuclear fallout level, reflecting less influence from nuclear reprocessing facilities (Figure 4.3). Highest values ($>1 \times 10^{10}$ atoms/L) are restricted along the 50-70°N bands and near to the vicinity of two point sources in Western Europe. Relatively higher levels could be also found in the Arctic Ocean and Nordic Seas region where the average $^{129}$I is $1 \times 10^9$ atoms/L, about 100 times above nuclear weapons testing fallout value, with a gradual decrease to $\sim 1 \times 10^8$ atoms/L in the northwest of Atlantic Ocean. $^{129}$I concentrations in south of 40°N in Northern Hemisphere decrease abruptly, ranging from $\sim 10^6$ to $\sim 10^8$ atoms/L which is generally 2-3 orders of magnitude lower compared to north of 40°N.
Concentration of $^{129}$I in the Nordic Seas and the Arctic Ocean clearly reflects main $^{129}$I pathways after its release from Sellafield and La Hague. $^{126}$I carried by the Norwegian Coastal Current (NCC) further mixed with the North Atlantic Current (NAC) into the Norwegian Sea and the Arctic Ocean, resulting in a dramatic increase of $^{129}$I ($\sim 3.5 \times 10^{10}$ atoms/L) along the Norwegian coast. A small part of the NCC westward current combined with water masses from southeastward branch of East Greenland Current (EGC) contribute to an enhanced level of $^{129}$I in the Norwegian Sea ($\sim 1.5-10 \times 10^{8}$ atoms/L). Concentrations in western Nordic Seas are normally one order of magnitude lower than east, surface $^{129}$I concentrations in the Greenland Sea and EGC are typically $5-10 \times 10^{8}$ atoms/L, with higher levels above the eastern Greenland shelf and decrease towards the central Greenland Gyre. Within the Arctic Ocean, the $^{129}$I-bearing water enriched in the Barents and Kara Seas moves along the continental margin, with a small component entering the
Canadian Basin and undergoing further bifurcation at Chukchi Plateau, whereas a large part returns along the Lomonosov Ridge and flows out of the Arctic through Fram Strait. This near continental high $^{129}$I flow seems not to incorporate into the fresher Siberia Coastal Current eastward towards Chukchi Sea because a remarkable $^{129}$I gradient is observed, suggesting an encounter of the Pacific- and Atlantic-origin water masses within the Chukchi Sea.

4.2 Variations of iodine ($^{127}$I and $^{129}$I) and its species along the 2010 transect

4.2.1 Iodine isotopes species in the North Sea

The concentrations of total iodine in the North Sea range from 0.31 to 0.41 μM with an average of 0.37 μM (Figure 4.4a). Maximum $^{127}$I appears in the Southern Bight whereas the distinctly lowest iodine concentration occurs off the coast of the West Frisian Islands, Netherlands. Iodate concentrations generally follow the same pattern as that of total iodine, which decrease to the lowest level of 0.20 μM from the German Bight to the Dutch coast, and then increase up to 0.35 μM in southern seawater samples. Iodide ranges between 0.06 and 0.18 μM in the surface waters, although the average concentration (0.11 μM) is markedly lower than the predominant species of iodate. The highest iodide value is observed close to the Dutch coast.

The results of $^{129}$I and its species ($^{129}$I$^{-}$ and $^{129}$IO$_3^-$) in the North Sea show a rather similar pattern, with a significant increase from 54°N to 52°N (Figure 4.4b). The concentrations of $^{129}$I indicate a nearly two orders of magnitude variation along the transect, ranging from $9.21\times10^9$ to $2.45\times10^{11}$ atoms/L with an average of $8.15\times10^{10}$ atoms/L. Higher values of over $2\times10^{11}$ atoms/L occurred in the south close to the Dover Strait, whereas the low concentrations around $1\times10^{10}$ atoms/L was observed in the north part of the sampling campaign, relatively distant from the English Channel. The distributions of $^{129}$I species depict a similar behavior with that of total $^{129}$I, and the concentrations of $^{129}$IO$_3^-$ (3.2×10$^9$-1.5×10$^{11}$ atoms/L) show a relatively wider range than $^{129}$I$^{-}$ (6.9×10$^9$-1.2×10$^{11}$ atoms/L). It is worthwhile to observe that compared to speciation of $^{127}$I, iodide is generally the dominant species of $^{129}$I in most samples, except the two in the south.

Similar to the pattern of $^{129}$I, values of $^{129}$I/$^{127}$I atomic ratio increased by almost two orders of magnitude from north to south (4.4×10$^{-8}$ to 1.0×10$^{-6}$) with an average of 3.5×10$^{-7}$ (Figure 4.4c). For species of $^{129}$I/$^{127}$I, the average levels of $^{129}$I$^{-}$/127I and $^{129}$IO$_3^-$/127IIO$_3^-$ are 5.9×10$^{-7}$ and 2.7×10$^{-7}$, respectively. The atomic ratios of $^{129}$I/$^{127}$I for iodide along the transect are all higher than that of $^{127}$I, as well as iodate, even in southern samples which have relatively high $^{129}$I-iodate concentration.
Both of measured $^{129}$I concentration and $^{129}$I/$^{127}$I ratio are 5-6 orders of magnitude higher than pre-anthropogenic levels, and 1-4 orders higher than values reported in any other oceans (He et al., 2013). Extremely high $^{129}$I concentrations in Southern Bight were clearly linked to the English Channel water (one branch of the North Atlantic Water), this water is mixed with the relatively low $^{129}$I of the North Sea water and is diluted as the water parcel moves northward along the continental coast in a short distance. A nearly 20-fold decrease of $^{129}$I concentrations appeared in the German Bight and the level remained rather constant (~$1 \times 10^{10}$ atoms/L).

Concentrations of $^{127}$I varied to a much lesser extent than $^{129}$I. Most of the $^{127}$I concentrations are comparable with other North Sea data, but generally lower than those reported in any other oceans (Elderfield and Truesdale, 1980; Hou et al., 2007; Michel et al., 2012). This is probably caused by discharge of fresh riverine water from the UK and the European continent in the south, as well as brackish water from the Baltic Sea through the Kattegat in the north. Moreover, the abundance of phytoplankton biomass inhabiting in
this temperate shallow shelf sea, especially in the Southern and German Bights, imply a potential organisms uptake of iodine in the North Sea (Joint and Pomroy, 1993). A positive correlation between salinity and the $^{127}$I concentration ($r = 0.62$, $P < 0.05$) was observed in all seawater samples investigated here. This feature also suggests that continuous dilution of saline and high iodine content of Atlantic water by continental runoff occurred from south to the north. Compared to total $^{127}$I, the species (iodide and iodate) show a considerable variation. The lowest total $^{127}$I concentration was observed close to the west Wadden Sea, which might demonstrate a relatively strong influence from the fresher west Wadden Sea (Zimmerman, 1976). This feature is also confirmed by lowest salinity and low iodate content in this sample.

4.2.2 Iodine isotopes species in the English Channel

Higher concentration of total iodine was observed in the English Channel compared to that in the Celtic Sea (mean 0.38 μM), particularly in the southwestern part (off Plymouth), where the average iodine concentration reaches 0.48 μM. In contrast, concentrations of iodate is generally increased from east to west along the transect and do not show pronounced variation between the Channel water and the open sea. Although salinity data is not available for some of the samples located in the Celtic Sea, the rationalized iodate (normalized to a salinity of 35) was rather constant (around 0.33 μM) west of La Hague. High iodide and $^{127}$I/$^{127}$IO$_3^-$ in the English Channel suggest a more productive water compared to the Celtic Sea, which is confirmed by high concentration of chlorophyll $a$ (Gentilhomme and Lizon, 1997). Insignificant correlation between iodate and iodide ($r = -0.34$ and $P = 0.22$) and the nearly constant rationalized iodate concentration (0.33 μM) between the western English Channel and the open sea suggests that, to a large extent, the changes in iodine speciation within this region is not primarily a result of interconversions between iodate and iodide. Higher concentration of total iodine in the western English Channel seems directly linked to the elevation of iodide ($r = 0.89$, $P < 0.0001$; slope = 0.8) and thus the net increase of iodine is mainly attributed to direct addition of iodide in this area. However, no similar pattern was observed in $^{129}$I and its species. This is because the $^{129}$I is overwhelmingly influenced by the source point of La Hague in the English Channel, as well as a relatively long time for $^{129}$I to reach open sea equilibrium.
Both $^{129}$I concentrations and $^{129}$I/$^{127}$I in the English Channel are 4-5 orders of magnitude higher than pre-nuclear values. The changes of $^{129}$I and $^{129}$I/$^{127}$I along the transect show a rather similar trend that is continuously decreasing towards the west (Figure 4.5). There is a ‘great sink’ starting just west of the La Hague tip, as $^{129}$I concentrations dramatically drop from $\sim 10^{16}$ to $\sim 10^{8}$ atoms/L. This is attributed to the major Atlantic water pathway in the English Channel, which results in a much more serious contamination of seawater in the North Sea in the east rather than the Atlantic Ocean in the west. Within the English Channel, the highest $^{129}$I concentration ($4.6 \times 10^{11}$ atoms/L) did not occur in samples that are close to the La Hague tip, but in the surrounding area of the Dover Strait. This is due to that the sampling transect was slightly towards the British Isles and the major water movement along the Channel causes dispersion from the French to the British side of the Channel. The same pattern was also reported in studies of other radionuclides such as $^{125}$Sb, $^{134}$+137Cs and $^{90}$Sr (Herrmann et al., 1995; Bailly du Bois and Guégueniat, 1999).

![Image](image_url)

*Figure 4.5: Concentration of $^{129}$I in the English Channel and the southern Celtic Shelf in 2010.*

Similar to $^{127}$I, iodate in the English Channel is the dominant species for $^{129}$I with a few exceptions, and this observation can generally be extended to the Celtic shelf (Figure 4.6). However, the ratio of iodide to iodate for $^{129}$I is quite different when compared with that of $^{127}$I. All of the $^{129}$I/$^{129}$IO$_3^-$ values...
were significantly higher than the corresponding $^{127}\text{I} / ^{127}\text{IO}_3^-$, which may be attributed to the presence of ‘old’ $^{129}\text{I}$ that reached its species equilibrium. This is because the major source of $^{129}\text{I}$ in the English Channel originated from La Hague and thus the observed $^{129}\text{I} / ^{129}\text{IO}_3^-$ should directly reflect the proportion of $^{129}\text{I}$ species in liquid discharges. It is worthwhile to mention that the average $^{129}\text{I} / (^{129}\text{IO}_3^- + ^{129}\text{I})$ in the English Channel in 2010 (0.43) is comparable to that in 2005 (0.41), though the data available in 2005 were sparse (Hou et al., 2007). This finding is vital for the estimate of $^{129}\text{I}$ redox rate in marine water as the percentage of $^{129}\text{I}$ in the source water could be regarded constant. Moreover, there was no significant difference for $^{129}\text{I} / (^{129}\text{IO}_3^- + ^{129}\text{I})$ in the west and east of the English Channel ($P=0.054$) in 2010. Despite more than one order of magnitude lower $^{129}\text{I}$ concentration west of La Hague, this feature again confirms that the western English Channel has also significantly been contaminated by the La Hague discharges and that the oxidation of iodide is a slow process within the English Channel. Compared to the data presented here, up to 20 times higher $^{129}\text{I} / ^{129}\text{IO}_3^-$ values were reported in the offshore of Fukushima surface water that was contaminated by the Japanese nuclear power plant (NP) accident in March 2011 (Hou et al., 2013). This suggests that a higher $^{129}\text{I} / ^{129}\text{IO}_3^-$ level is always expected in discharges of $^{129}\text{I}$ through anthropogenic nuclear activities and evidently, different NRFS/NPs have different initial $^{129}\text{I} / ^{129}\text{IO}_3^-$ values in their source waters.

Figure 4.6: Ratio of iodide/iodate for $^{129}\text{I}$ and $^{127}\text{I}$ in the English Channel and the southern Celtic Sea in 2010.
4.2.3 Iodine isotopes species in the northeastern Atlantic Ocean

It is apparent that, as a sensitive radioactive tracer, the concentration of $^{129}$I (including $^{129}$I$^{-}$ and $^{129}$IO$_3^{-}$) shows a larger variation in the seawater compared with that of $^{127}$I (Figure 4.7). More than one order of magnitude difference in $^{129}$I concentration is shown in the northeastern Atlantic where the highest occurred in the middle of Biscay Bay ($12.67 \times 10^8$ atoms/L) and all the $^{129}$I data here are higher than $4.0 \times 10^7$ atoms/L. Five pronounced peaks of $^{129}$I (>2×10$^8$ atoms/L) are observed along the surface water transect. However, if these distinct peaks are not taken into consideration, average concentration of $^{129}$I in the sampled transect is less than $1 \times 10^8$ atoms/L (mean $6.9 \times 10^7$ atoms/L) and also does not vary a lot in the open sea surface water. Despite nearly similar behavior for $^{129}$I$^{-}$ and $^{129}$IO$_3^{-}$ in the sampled surface water, the concentrations of $^{129}$I$^{-}$ show a relatively wider range ($0.07$-$5.73 \times 10^8$ atoms/L). Additionally, $^{129}$IO$_3^{-}$ concentrations are normally higher than that of $^{129}$I$^{-}$ in the sampled region with a few exceptions. The isotopic ratio of $^{129}$I/$^{127}$I has the same trend as that of $^{129}$I, which varies between $1.82 \times 10^{-10}$ and $5.69 \times 10^{-9}$ with an average value of $6.63 \times 10^{-10}$. The same pattern also appears for the ratio of $^{129}$I$^{-}$/$^{127}$I and $^{129}$IO$_3^{-}$/$^{127}$IO$_3^{-}$ and the atomic ratios of $^{129}$I/$^{127}$I for iodide is significantly higher than those for iodate in the investigated region.

![Figure 4.7: Iodine isotopes ($^{127}$I and $^{129}$I) and their species in the Atlantic seawaters. (a) Variations of isotopic ratio of $^{129}$I/$^{127}$I, $^{127}$I$^{-}$/$^{129}$I$^{-}$ and $^{127}$IO$_3^{-}$/$^{129}$IO$_3^{-}$ in the sampled transect along the northeastern Atlantic Ocean. (b) Concentration of $^{129}$I and its species ($^{129}$I$^{-}$ and $^{129}$IO$_3^{-}$) along the sampled transect in the northeastern Atlantic Ocean. The error bars show the analytical uncertainty of one sigma.](image)

Higher values of $^{129}$I$^{-}$/^{129}$IO$_3^{-}$ compared with $^{127}$I$^{-}$/^{127}$IO$_3^{-}$ are found in all seawater samples (Figure 4.8). Some $^{129}$I$^{-}$/^{129}$IO$_3^{-}$ values, however, are close to the corresponding $^{127}$I$^{-}$/^{127}$IO$_3^{-}$ levels which are interpreted to reflect a local effect. This may either be related to older water ventilated to the surface during winter, or the small-scale accelerated redox cycle induced by local
chemical or biological characters in these waters. The $^{129}$I/$^{129}$IO$_3^-$ value varies from 0.14 to 2.02 in samples where the highest level is located in the region between Madeira and the African coast. Most of the ratio for $^{129}$I lies at 0.3-0.7 while the $^{127}$I/$^{127}$IO$_3^-$ ratio is normally below 0.2. High values of $^{129}$I/$^{129}$IO$_3^-$ (above 0.7) are thought to be directly linked to the large-scale circulation pattern as described in the next section. Similar to $^{129}$I and $^{129}$I/$^{127}$I, there are five peaks observed for $^{129}$I/$^{129}$IO$_3^-$ which shows decreasing values towards the north. Unlike the $^{129}$I/$^{129}$IO$_3^-$, the ratios of iodide to iodate for $^{127}$I remain nearly constant in the sampled surface water transect. On average the value for $^{127}$I/$^{127}$IO$_3^-$ is 0.14, which is a factor of five lower than that of $^{129}$I/$^{129}$IO$_3^-$ (0.65).

![Figure 4.8](image_url)

*Figure 4.8: Variations of $^{129}$I/$^{129}$IO$_3^-$ and $^{127}$I/$^{127}$IO$_3^-$ along the sampled transect of the northeastern Atlantic Ocean. Colored zones represent $^{129}$I species in samples that is close to (< 0.3, pink), approaching (0.3-0.7, green) and far from reaching (> 0.7, yellow) the iodine redox equilibrium in seawaters.*

Concentrations of $^{129}$I show about 30 times difference in surface seawater and with an average of $1.53 \times 10^8$ atoms/L in the sampled transect in 2010. In addition, the ratio of $^{129}$I/$^{127}$I also shows a 30 times variation between the low and high values ($1.82-56.85 \times 10^{-10}$ atoms/atoms). Both of these values are 2-4 orders of magnitude higher than the natural $^{129}$I levels in the ocean (estimated at $\sim 10^2$ atoms/L for $^{129}$I and $\sim 10^{-12}$ for $^{129}$I/$^{127}$I), which implies strong influence of anthropogenic nuclear activities along the European Coasts. Accordingly, our data suggest that, even the lowest $^{129}$I value measured ($4.3 \times 10^7$ atoms/L and $1.82 \times 10^{-10}$ atoms/atoms for $^{129}$I/$^{127}$I ratio) is higher
than the background level of the nuclear weapon testing. This again indicates that the surface water of the northeastern Atlantic Ocean had been labeled by a nuclear fuel reprocessing signal, either from direct marine discharge or from atmospheric $^{129}$I releases. In general, iodate is the dominant species of dissolved iodine for both $^{127}$I and $^{129}$I in the surface waters of the sampled northeastern Atlantic. More than 75% of $^{127}$I-iodate is observed in these surface waters, which is comparable to seawaters collected in any other ocean regions (Tsunogai and Henmi, 1971; Truesdale, 1978; Elderfield and Truesdale, 1980; Jickells et al., 1988; Wong, 1995; Campos et al., 1996; Wong and Cheng, 1998; Campos et al., 1999; Farrenkopf and Luther III, 2002; Waite et al., 2006; Bluhm et al., 2011). However, for the species of $^{129}$I, there is evidently a higher concentration of iodide compared to that of $^{127}$I. This huge discrepancy of iodine species for $^{127}$I and $^{129}$I probably reflects different sources of iodine isotopes.

4.3 Sources of $^{129}$I

4.3.1 Sources of $^{129}$I in the North Sea

Considerable variation of iodide/iodate values for $^{129}$I in the North Sea was observed compared with that for $^{127}$I. This feature implies a reduction of iodate in the North Sea as the English Channel water parcels moves northward. Despite the positive correlation between $^{127}$I and salinity, the insignificant correlation between iodide and salinity indicates that part of the $^{129}$IO$_3^-$ is locally reduced. All these features provide evidence for a reductive environment within the North Sea, possibly mediated by bio-activities.

An earlier study (Hou et al., 2007) reported a rapid reduction of $^{129}$IO$_3^-$ in the continental European coastal areas and the German Bight. $^{129}$I$^-$/$^{129}$IO$_3^-$ values as high as 50 were observed in the estuary of Elbe River and they related this feature to the combination of chemical and biological processes. Our samples were generally located in the open North Sea, distant from the coastline. Therefore, a significant part of $^{129}$I$^-$ found in our northern samples might be associated with diffusion and transportation of $^{129}$I$^-$-rich water that originated from coastal areas, particularly from the hypoxic German Bight. The differences between $^{129}$I/$^{127}$I isotopic ratios for iodide and iodate are significantly larger in the southern samples than those in the north. This feature indicates that the major source of $^{129}$I$^-$ in northern samples was water masses bringing other than local production.

The west Wadden Sea is also a shallow area with estuarine properties characterized by relatively low salinity and large loading of organic matter. Additionally, very low oxygen saturation on its tidal mudflat was reported and seasonal episodic oxygen deficiency occurred in its interior basin (Van
der Veer and Bergman, 1986; Hoppema, 1991). Thus the western Wadden Sea should be another potential source of newly produced \[^{129}\text{I}\]-iodide under anoxic conditions and further investigation of \[^{129}\text{I}\] within this region is needed.

### 4.3.2 Sources of \[^{129}\text{I}\] in the northeastern Atlantic Ocean

For the \[^{129}\text{I}\] inventory, the influence of direct marine discharges and later transport by ocean current systems play a major role for the concentration in the surface water of the investigated area. The \[^{129}\text{I}\] concentration and \[^{129}\text{I}/^{127}\text{I}\] value in samples north of Cape Finisterre (Spain) analyzed here also confirm the influence from north, where a gradually decreasing pattern is documented southward. Therefore, the \[^{129}\text{I}\] level in the north part of the investigated region exhibited a combined contribution from Sellafield and La Hague that could be further advected southward.

Seawaters with high \[^{129}\text{I}\] concentration south of 40°N clearly imply a different source other than the influence of Sellafield and La Hague from the north. These three isolated peaks do not seem linked to waters from the north due to the general pattern of meridional water movement with respect to the Portugal Current system in this region (Fiúza et al., 1998). This is also confirmed by speciation analysis of \[^{129}\text{I}\] that shows in the southern three peaks, iodide as the main species in the surface water column.

In addition to the two NRFs mentioned above, the Marcoule NRF (France), which is located on the banks of Rhone river, directly released 45 kg of liquid \[^{129}\text{I}\] to the river and 145 kg of \[^{129}\text{I}\] to the atmosphere during its operation until 1997 (Hou et al., 2009b). Considering 50% of atmospheric \[^{129}\text{I}\] deposited in the vicinity of the plant and assume all \[^{129}\text{I}\] has eventually injected into the Mediterranean Sea through continent runoff, about 120 kg of \[^{129}\text{I}\] was calculated in the Mediterranean Sea. As a result, the average concentration of \[^{129}\text{I}\] would be about \(1.5\times10^8\) atoms/L if the \[^{129}\text{I}\] is homogeneously mixed in the Mediterranean water. Considering the large amount of \[^{129}\text{I}\] released by Marcoule reprocessing plant and the relatively long residence time of iodine (~1800 y) compared with the water turnover time (~1000 y) in the Mediterranean Sea, the Mediterranean water could be a source of \[^{129}\text{I}\] to the North Atlantic Ocean. Seawater and algae samples taken from the Mediterranean Sea show a comparable \[^{129}\text{I}\] level with our samples that show high \[^{129}\text{I}\] level in the south, suggesting a Mediterranean origin of these waters (Osterc and Stibilj, 2008; Pham et al., 2010). To our best knowledge, there is no \[^{129}\text{I}\] speciation in the Mediterranean Sea. However, \[^{129}\text{I}/^{129}\text{IO}_3^-\] values in the English Channel suggest that the source water of \[^{129}\text{I}/^{129}\text{IO}_3^-\] from nuclear reprocessing facilities should contain high values (Hou et al., 2007) and it is reasonable to conclude a high \[^{129}\text{I}/^{129}\text{IO}_3^-\] in the Mediterranean water. Moreover, high iodide concentration is normally found in coasts, bays, estuaries and semi-enclosed basin (Wong, 1995; Tian et al., 1996; Hou et al.,
Therefore, seawater samples south of 40°N that are characterized by high $^{129}\text{I}$ and $^{129}\text{I}/*^{129}\text{O}_3^-$ may represent direct influence from the Mediterranean overflow plume that was captured during the cruise.

![Figure 4.9: Concentrations of $^{129}\text{I}$ (10$^8$ atoms/L) along the transect and suggested surface $^{129}\text{I}$ pathways from the English Channel and the Strait of Gibraltar (dashed line). Red regions represent major coastal upwelling and solid blue lines show the spreading pathways of deep Mediterranean water. The nuclear reprocessing facilities (NRFs) are marked as stars.](image)

We suggest that the surface waters at 36.5°N may reflect the propagation of a branch of this onshore water westwards towards the open ocean after leaving Cape St. Vicente when easterlies dominated (Figure 4.9). Moreover, a poleward surface current has been reported off the west coast of Portugal during winter when the wind is blowing northward (Frouin et al., 1990). When this water reaches the Cape Espichel, local coastal morphology, shelf/slope bathymetry as well as propagation of eddies make the $^{129}\text{I}$ plume extend seaward. The other two high-$^{129}\text{I}$ samples, which occur in the middle
of Madeira and African coast, however, are related to the onshore flow of the Canary Current, which with its one branch separated from the northern Morocco coast (Johnson and Stevens, 2000), may transport $^{129}\text{I}$ from the Strait of Gibraltar to further west around 14°W.

### 4.4 $^{129}\text{I}$ inventories in the North Sea and the English Channel

Here we made a simple calculation of $^{129}\text{I}$ inventory based on data from 2005 (Michel et al., 2012) and applying the release function from the NRFs (Figure 1.2). The entire North Sea is divided into three compartments and for the relatively deep regions (i.e. the Norwegian Trench and the central and northern part of the North Sea), the compartments are subdivided into two layers separated by mean thermocline depth of 30 m. Distribution of $^{129}\text{I}$ inventory in each 10×10 km water column is shown in Figure 4.10. The results show that about 114 kg $^{129}\text{I}$ resided in the North Sea water. Among this, more than 90% of $^{129}\text{I}$ inventory resides in the German Bight and the southern North Sea.

![Figure 4.10: Distribution of gridded $^{129}\text{I}$ inventory (in 10^{22} atoms) in the North Sea in 2005.](image)

$^{129}\text{I}$ inventories in the central and northern portion of the North Sea were more than two times higher than that in the Norwegian Trench and >90% was accumulated in the upper layer whereas in the Norwegian Trench, the
$^{129}$I inventory is comparable in surface and deep layers. However, inventories of gaseous (atmospheric) $^{129}$I release only account for 5% and 4% of the liquid (marine) discharges from Sellafield and La Hague until 2005, respectively. These percentages were even decreased to < 3% and < 1% in the recent five years, respectively. Therefore, atmospheric release of $^{129}$I is relatively insignificant compared to the marine discharge. Accordingly, the estimated $^{129}$I inventory in the North Sea accounts for about 3.4% of the individual La Hague marine discharges, and 2.4% of the combined marine discharges from La Hague and Sellafield until 2005.

During 2006-2010, the $^{129}$I marine discharges from La Hague were 956 kg, which will add about 32.5 kg of $^{129}$I to the inventory in the North Sea until 2010 based on the estimated 3.4% mentioned above. Thus if we simply ignored the $^{129}$I contribution from Sellafield and the loss of $^{129}$I to the Baltic Sea in 2010, $^{129}$I inventory in the North Sea would be 147 kg until 2010.

For inventory calculation of the English Channel, gridding with 10 km×10 km and subdivision into western and eastern parts was applied. The relatively deep western English Channel is further subdivided into two layers separated by mean thermocline depth of 20 m. The estimated inventory of $^{129}$I in the English Channel is $78 \pm 12$ kg, in which over 90% resides in the east of La Hague (Figure 4.11). The inventory in the western English Channel, however, is much less. Even when the well mixed water column in the whole western part is considered, the inventory in the west English Channel is still only one-fifth of that in the east. Additionally, though the volume of the surface layer is nearly three times less than that in the bottom, it accounts for about 84% of the total inventory of the western part. Apart from total $^{129}$I, a first inventory estimation of $^{129}$I species in the English Channel is also calculated. Despite the high $^{129}$I/$^{129}$IO$_3^-$ that occasionally occurred in some seawater samples, most of the inventory is iodate-dominated in the English Channel. Furthermore, distribution and proportion of $^{129}$I and $^{129}$IO$_3^-$ in each compartment generally follow the same pattern as total $^{129}$I. This distribution behavior of $^{129}$I and its species agrees well with the major water movement within the channel.

Direct marine release from La Hague plays a major role in terms of $^{129}$I inventory in the English Channel and the estimated $^{129}$I in 2010 constitutes 1.77% of liquid release by La Hague since the start of its operation until 2010. Compared to neighboring areas, the inventory of $^{129}$I in the English Channel is nearly 4 times higher than that in the Baltic Proper (Yi et al., 2010), but about half of the estimated inventory in the North Sea.
In general, there is a total of 255 kg of $^{129}$I in the English Channel, North Sea and the Baltic Sea, which constitutes only 5.8% of marine discharges from La Hague. This feature implies that most of $^{129}$I released from La Hague has left the North Sea and partly resides in the sediments.

4.5 Transformation among iodine species in seawater

In marine waters, iodine mainly exists as iodate, iodide and a minor fraction dissolved organic iodine (DOI). In the state of thermodynamic equilibrium, iodate should be the only detectable form of iodine in oxygenated seawater. However, significant iodide is often observed in the ocean surface layer. In some coastal bays, or anoxic basins such as the Baltic Sea and the Black Sea,
iodide could be the major form (Ullman et al., 1988; Luther III and Campbell, 1991; Luther III et al., 1991; Truesdale et al., 2001). Concentration of iodine species varies a lot with respect to depth and locations in the sea. Although the conversion between iodine species in natural water is not well understood, it might be attributed to chemical, biological and photochemical processes.

Several abiotic mechanisms have been suggested to reduce iodate to iodide under anoxic conditions, with the presence of reducing agents such as iron, manganese and sulfur species (e.g. thiols, bisulphides, etc.) (Jia-Zhong and Whitfield, 1986; Anschutz et al., 2000):

$$\frac{1}{2} \text{Mn}^{2+} + \frac{1}{6} \text{IO}_3^- + \frac{1}{2} \text{H}_2\text{O} \leftrightarrow \frac{1}{2} \text{MnO}_2 + \frac{1}{6} \text{I}^- + \text{H}^+$$

Photochemical reduction of iodate may also be important which was supported by laboratory experiments (Spokes and Liss, 1996) and this process seems strongly catalyzed by dissolved organic matter:

$$\text{IO}_3^- + 6\text{H}^+ + 6\text{e}^- + \text{hv} \rightarrow \text{I}^- + 3\text{H}_2\text{O}$$

The presence of iodide in the oxic euphotic zone is suggested by reduction of iodate mediated biologically. These biotic processes include bacterial reduction with the enzyme nitrate reductase (Tsunogai and Sase, 1969; Wong and Hung, 2001), and the phytoplankton activities (Moisan et al., 1994; Tian et al., 1996; Wong et al., 2002). The reduction of iodate to iodide does not seem to be related to concentration of primary production but more linked to cell senescence (Tian et al., 1996; Bluhm et al., 2010). In addition, iodide may be released from sediment at the sediment/seawater interface where remineralization of organic materials is intensified (Ullman and Aller, 1980; Aldahan et al., 2007):

$$\text{C-H-O-N-I} + \text{SO}_4^{2-} \rightarrow \text{CH}_4 + \text{CO} + \text{H}_2\text{S} + \text{NO}_x + 2\text{I}^-$$

Conversely, some experiments by laboratory cultures argued that neither the photochemical process nor organic activity were a substantial effect on iodate reduction. In these experiments, little change of iodine species was reported under phytoplankton bloom or high light intensity conditions (Brandão et al., 1994; Wong et al., 2002; Truesdale et al., 2003). Thus a hypothesis was proposed that iodate may be used to mop up electrons which present in excess of photosynthetic needs (Waite and Truesdale, 2003).

When the iodide is produced, then oxidation into iodate is sluggish, because the redox of iodine in marine waters is suggested to be a slow process. The mechanisms that govern the iodide oxidation are still unclear. Photochemical oxidation may occur with the help of strong UV radiation or oxidants (e.g. H$_2$O$_2$, O$_3$, etc.) (Wong and Zhang, 2008):
\[
2\Gamma + 1/2 \text{O}_2 + \text{H}_2\text{O} \stackrel{h\nu}{\rightarrow} \text{I}_2 + 2\text{OH}^-
\]
\[\Gamma + \text{H}_2\text{O}_2 \rightarrow \text{HOI} + \text{OH}^-\]

The reactive transients of \(\text{I}_2\) and \(\text{HOI}\) tend to return to \(\Gamma\) or incorporated into organic materials rather than the further oxidation of \(\text{HOI}\) to iodate. Therefore, the transformation of iodide to iodate in seawater might also be biologically mediated (Luther George et al., 1995).

The significant quantities of dissolved organic iodine (DOI) in some coastal and estuarine waters may add a new loop of iodine geochemistry in seawaters (Wong and Cheng, 2001). DOI can be formed from iodate and iodide with reactive oxidants, or released from decomposition of organic matter. Conversely, decomposition of DOI can introduce iodide to the water column and this process was suggested to be photochemical or biological (bacterial mediated) (Luther Iii et al., 1991; Luther George et al., 1995; Wong and Cheng, 2001b).

In most of our seawater samples along the transect, although iodate confirmed to be predominantly occurring, significant iodide can also be observed, particularly in the North Sea and the English Channel. This is in accord with previous reports and it is likely influenced by biotic processes. However, since the redox of iodine is suggested to be a slow process, it seems that relatively large variations of iodine species composition in some regions, such as the North Sea and the southwestern English Sea, mainly reflect water mass mixing and migration rather than interconversions between iodine species. For \(^{129}\text{I}\), in most cases high \(\text{^{129}I}^-/\text{^{129}IO}_3^-\) were found, especially in the eastern North Sea, compared to \(\text{^{127}I}^-/\text{^{127}IO}_3^-\). This behavior is attributed to propagation of inshore waters that bear a high concentration of \(^{129}\text{I}^-\) into the German Bight, where strong iodate reduction happens. High \(^{129}\text{I}^-\) in some Atlantic water samples may also occur through reduction in the coastal areas of the northwest Mediterranean Sea, which might be driven by mixed mechanisms mentioned in this section. In addition, DOI may play an insignificant role since the values of \((\text{^{129}I}^- + \text{^{129}IO}_3^-)/\text{^{129}I}\) in all samples range between 0.90 and 1.10, which lie within the analytical error range. Moreover, in open seas, DOI content is normally low and this was confirmed by seawater samples taken from the North Sea (Hou et al., 2013).
5. Environmental impact of $^{129}$I

At present, $^{129}$I is not regarded to pose a significant human health risk. However, because of its high mobility and long half live, as well as the fact that more than 90% of spent nuclear fuel is still waiting for reprocessing, concentrations of anthropogenic $^{129}$I are expected to increase in the studied regions. Due to its low beta-decay energy, $^{129}$I may not constitute a significant external exposure hazard. Soils from Sweden indicated about 1.0 Bq/m$^2$ for $^{129}$I, which was much less radioactivity than that from $^{137}$Cs (10$^3$-10$^5$ Bq/m$^2$) (Aldahan et al., 2006). However, elevated levels of $^{129}$I in water, atmosphere and soil will finally find its way into the food chain, which can result in internal exposure effects.

Iodine is generally concentrated in organisms which are associated with the human diet. Osterc et al. (Osterc and Stibilj, 2012) investigated $^{129}$I concentrations in mussel tissues collected in the Mediterranean Sea and their results showed a high $^{129}$I/$^{127}$I values (10$^{-9}$-10$^{-8}$). A wider ratio range (10$^{-11}$-10$^{-8}$) was observed in milk from central USA (Oliver et al., 1982). It is known that seaweed can concentrate iodine to extremely high levels, and the $^{129}$I/$^{127}$I is normally higher than 10$^{-8}$ in seaweeds sampled from western and northern European coast (Hou et al., 2000a; Yiou et al., 2002; Keogh et al., 2007). The bioavailability of iodine depends on its species in the environment. Water soluble and exchangeable fractions of $^{129}$I in soil are preferentially taken up by plants (Hou et al., 2009b). For mammals and human beings, KI is more easily assimilated than iodine bonded to organic macromolecules (Hou et al., 2009b). Although most of iodine uptake is relatively quickly excreted out of human body (4-5 months), the transformation path is commonly through the mammal thyroid (Hou et al., 2009b; Jahreis et al., 2001). $^{129}$I/$^{127}$I in animal (or human) thyroid present a low level of ~10$^{-10}$-10$^{-9}$ in areas far from known-$^{129}$I sources, such as NRFs and the Chernobyl region (Chao and Tseng, 1996; Handl, 1996; Hou et al., 2000b). Accordingly, much lower values of $^{129}$I/$^{127}$I that are close to pre-anthropogenic level were reported from Argentina (Negri et al., 2012). However, in Chernobyl fallout regions or vicinity areas of NRFs, the $^{129}$I/$^{127}$I ratio dramatically increased to 10$^{-3}$-10$^{-5}$ (VanMiddlesworth and Handl, 1997; Fréchou et al., 2002). Considering about 10 mg of iodine in human thyroid, the highest $^{129}$I/$^{127}$I ratio of ~10$^{-5}$ (0.65 Bq of $^{129}$I) results in equilibrium annual dose equivalent to the thyroid of ~10$^{-2}$ mSv/y (Soldat et al., 1973). This is about two orders of magnitude lower than annual maximum effective dose for an adult which is
the suggested permissible level of European Nuclear Society (1mSv/y) (http://www.euronuclear.org/info/encyclopedia/d/doselimitvalue.htm).

The $^{129}$I in table salts that are used in Sweden varies at 1-4×10$^{-6}$ Bq/kg (Aldahan et al., 2006), which is equivalent to 7.3-29.2×10$^{-7}$ Bq/y if we assume 2 g of daily uptake of salt, thus the radioactivity from daily table salt can be neglected. Similarly, insignificant radiation of $^{129}$I through inhalation is estimated (10$^{-7}$-10$^{-6}$ Bq/y) if the average $^{129}$I concentration of 10$^{-4}$-10$^{-5}$ atoms/m$^3$ in atmosphere is applied (Santos et al., 2005). However, it is radioactive hazard of water due to large amount of daily water consumption possible (~2L/day for adult). Aldahan et al. (Aldahan et al., 2006) reported that $^{129}$I in Swedish tap water is ~10$^8$ atoms/L. Therefore, daily intake of $^{129}$I through drinking water is 2×10$^8$ atoms and the corresponding radioactivity is 200 times higher than that from table salt and inhalation. These features suggest an insignificant radiation hazardous presently contributed by $^{129}$I intake.

Concentration of $^{129}$I in seawaters collected in the northeastern Atlantic Ocean was slightly lower than in the tap water in Sweden, while the water samples taken from the North Sea and the English Channel showed a much higher $^{129}$I level (1×10$^{-5}$ – 6×10$^{-4}$ Bq/L). However, the external radiation of $^{129}$I is less harmful because $^{129}$I is a soft beta-emitter. Thus, the potential radiological risk for human beings in the western European coast and the Baltic regions is accompanied with internal dose, when humans consume seafood which concentrates surrounding $^{129}$I to an extremely high level.

Fish otolith has been used as an environmental marker for fish lifetime and migration pathway (Campana, 1999). The majority of elements deposited in otolith originate from water, with a minor fraction coming from food sources. $^{127}$I was already found in otolith and since $^{129}$I has been detected in fish tissues and flesh (reference IAEA), $^{129}$I may also be incorporated into the otolith (Gemperline et al., 2002; Pham et al., 2006). Thus, variations of iodine isotopes ($^{129}$I and $^{127}$I) and their species in seawater are expected to be reflected in the growth of otoliths (e.g. Atlantic cod and Atlantic herring). This possibility can open a new interesting approach where growth and migration pathways of fish can be traced using the ratio of $^{129}$I/$^{127}$I.
6. Conclusions

This thesis concerns the distribution and sources of iodine isotopes ($^{127}$I and $^{129}$I) and their species (iodide and iodate) in ocean waters collected from the North Sea, the English Channel, the Celtic Sea and the northeastern Atlantic Ocean. Additionally, a review of $^{129}$I distribution in the oceans was performed. The main conclusions and findings are summarized below:

1. Concentrations of $^{129}$I in the world oceans range several orders of magnitude, but were all at least 130 times higher than the pre-nuclear era level. The highest values were restricted to the English Channel and the Irish Sea, whereas low levels occurred in regions that are far from major NRFs. Currently, most available oceanic $^{129}$I data come from areas north of 60°N in the Atlantic Ocean, Nordic Seas and the Arctic Ocean, while in most parts of the Pacific, Indian and Southern Oceans, data are insufficient which hinder tracking global oceanic distribution of $^{129}$I. Moreover, although it would be an additional powerful tool in iodine geochemistry, few $^{129}$I data on speciation of $^{129}$I was available for the world oceans.

2. A more than one order of magnitude difference in $^{129}$I concentrations was observed in the English Channel water between west and east of La Hague peninsula. This observation suggests strong impact of water movement towards the east and into the North Sea. The results show that $^{129}$I in the southern Celtic Sea is mainly originated from La Hague, although some clues implied influences from Sellafield.

3. In general, changes in the $^{127}$I and $^{127}$I$^-$/$^{127}$IO$_3^-$ are comparable to data from other marine waters which are related to natural distribution patterns. In addition, occurrence of deepwater upwelling in the western English Channel was detected through enhanced $^{127}$I concentration in surface water.

4. $^{129}$I inventories in the North Sea and the English Channel were estimated as 147 kg and 78 kg until 2010, respectively. Of these, more than 90% of $^{129}$I resides in the eastern English Channel, the southern North Sea and the German Bight. Total inventory of $^{129}$I in the Eng-
lish Channel, the North Sea and the Baltic Sea is about 255 kg, which constitutes only 5.8% of marine discharges from La Hague.

5. Iodate is the dominant iodine species for both $^{127}$I and $^{129}$I in most seawater samples from the North Sea to the Atlantic Ocean. Besides, iodide to iodate ratio for $^{129}$I was normally higher than that of $^{127}$I, which reflects different sources of the two isotopes. Temporal variation of $^{129}$I and its species in the North Sea show an off-shore propagation and dilution of coastal water, which can be coupled with interannual climate oscillation over this region.

6. The average value of $^{129}$I/(129IO$_3^-$ + $^{129}$I) in source water (English Channel) shows little temporal variation which was crucial for estimation of iodine species interconversion. Use of this constant ratio resulted in identifying water transport from the western English Channel via Biscay Bay as the main source of $^{129}$I in the northeastern Atlantic Ocean.

7. Speciation analysis of $^{129}$I suggests a slow process of $^{129}$I oxidation in the open sea, where about 9% of $^{129}$I is annually oxidized. This feature means that it takes at least 10 years for the $^{129}$I/129IO$_3^-$ pair to reach their natural equilibrium as the water is transported from the English Channel.

8. The results of $^{129}$I and its species suggest that the Mediterranean Sea is another source contributing to the inventory of $^{129}$I in the North Atlantic Ocean. Therefore, our research proposes a potential prospective of labeling MOW (Mediterranean Outflow Water) using $^{129}$I speciation. Depth profiles of $^{129}$I in the Gibraltar Strait and the Gulf of Cadiz are needed for further investigations.

9. The environmental impact of $^{129}$I can be a multi-axis tool, one is related to radioactivity hazards which is presently seems not harmful. The other axis is a potential tracer of water masses exchange and circulation. The third axis is a tool for ecosystem variability, where migration of fish and other marine species can be traced.
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8. Summary in Swedish

$^{129}\text{I}$ är en radioactive jodisotop med lång halveringstid som sedan 1940-talet tillförs miljön i stora mängder som en följd av antropogena verksamheter. Eventuella risker till följd av isotopens radioaktivitet är inte undersökta i detalj. $^{129}\text{I}$ har däremot framgångsrikt använts som spårämne i marina system för att undersöka havsströmmar, utbyte av vattenmassor, vattnets transportvägar och allmän jodgeokemi. Undersökningar av hur isotopen sprids i vatten har mestadels fokuserat på Nordsjön, de nordiska haven, Östersjön och Ishallivet eftersom de utgör potentiella transportvägar för $^{129}\text{I}$-utsläpp från de två stora kärnbränsleuppmättningsorganisationers anläggningar i Engelska kanalen (La Hague, Frankrike) och Irlandska Sjön (Sellafield, Storbritannien). Kunskaperna om $^{129}\text{I}$ i andra marina miljöer är dock fortfarande bristfälliga. I denna avhandling presenteras nya data om spridningsmönster och källor för $^{129}\text{I}$ i Atlanten genom analyser av ytvatten längst en transek från Nordsjön, genom Engelska kanalen, vidare in i Keltiska havet och genom nordöstra Atlantiska oceanen. Ytvattensprovtagningen genomfördes under oktober och november 2010, som en del av Svenska Polarforskningssekreteriets och amerikanska National Science Foundations (NSF) Antarktis expedition. Dessa prover analyserades både vad avser totala mängder av två jodisotoper ($^{127}\text{I}$ och $^{129}\text{I}$) samt deras olika kemiska former (jodat och jodid), med hjälp av en omfattande kemisk separation, följt av mätningar med accelerator masspektrometri (AMS) och induktivt kopplad plasma masspektrometri (ICP-MS).

Avhandlingen innehåller en sammanfattning av data om $^{129}\text{I}$ i världshaven (Paper I), där det framgår att $^{129}\text{I}$-konzentrationer i ytvatten från Atlanten, Stilla havet och Indiska oceanen är minst 1-3 magnituder lägre än i Ishallivet. Resultaten av provtagningarna på jodisotoper ($^{127}\text{I}$ och $^{129}\text{I}$) och deras kemiska former längs transeksen presenterade i fyra artiklar (Papers II-V). Av dessa analyser framgår att $^{129}\text{I}$-halten i havsvatten längs transeksen uppvisar en betydande förändring med en ökning på cirka 40 gånger från Nordsjön till Engelska kanalen, där det högsta värdet påträffades nära Doverkanalen. Denna höga $^{129}\text{I}$-halt följs av en dramatisk minskning på mer än fyra magnituder från Cap de La Hague till det öppna havet. Alla $^{129}\text{I}$-konzentioner och $^{129}\text{I}^{127}\text{I}$-kvoter i de insamlade ytvattensproverna låg över nivåerna för det globala nedfallet från kärnvapenprov.

Förutom analyser av $^{129}\text{I}$-konzentrationer och $^{129}\text{I}^{127}\text{I}$-kvoter, visar resultaten av jodisotopernas olika kemiska former på en ny möjlighet att förfina
användande av $^{129}$I som spårmärke i marina miljöer. Fram till idag har det endast funnits data som visar på bildande av de olika formerna av $^{129}$I i Nordsjön och Östersjön men i denna avhandling utökas denna viktiga information till andra havsområden. Tydliga geografiska källorområden för dessa två jodisotoper framträder av den stora skillnaden mellan jodid/jodat för båda $^{127}$I och $^{129}$I. Dessa karaktärsdrag antyder att den naturliga termodynamiska jämvikten mellan isotoperna inte föreligger i haven och att oxidationsprocessen där $^{129}$I omvandlas till $^{129}$IO₃⁻ är långsam i det öppna havet. Förändringen av $^{129}$I/$^{129}$IO₃⁻ i havsvatten kan således användas för att identifiera $^{129}$I-källor vilket i sin tur leder till slutsatsen att den huvudsakliga källan till $^{129}$I i nordöstra Atlanten kan hänföras till Keltiska havet och inte Labradorhavet. Skillnader i $^{129}$I/$^{129}$IO₃⁻ kvoten i proverna från Keltiska sjön tyder på en påverkan från utsläppen från Sellafields kärnbränsleupparbetning. Utsläppen från La Hague å andra sidan förefaller främst bidra till $^{129}$I i västra Engelska kanalen. Denna förekomst tillsammans med ett möjligt södergående vattenflöde från Irländska sjön, har medfört att Keltiska sjön kan ses som ett $^{129}$I-förorenat område. Om en $^{129}$I-plym förflyttar sig ytterligare, vid gynnsamma vindförhållanden, kan den även komma att påverka nordöstra Atlanten och då särskilt Biscayabukten.

Höga $^{129}$I/$^{129}$IO₃⁻ halter i havsvatten från södra Nordsjön visar på en icke kustnära spridning av europeiska kustvatten, vilket kan vara kopplat till extremä klimatvariationer. De observerade $^{129}$I/$^{129}$I värdena från Engelska kanalen ger en tydlig bild av de troliga ingångsvärdena till La Hagues avloppslagringar och proportionerna visar på små temporala inom kanalen. Fem vattenprover från nordöstra Atlanten karakteriserades av höga $^{129}$I-koncentrationer och skillnader i $^{129}$I/$^{129}$IO₃⁻ halten att dessa vattenmassor kan förklaras med att olika källorområden föreligger, där de norra proverna associerades med utsläpp från Sellafield och La Hague medan de övriga proverna antyder Medelhavsvatten som källa till $^{129}$I. Förslagvis kan $^{129}$I och dess kemiska former ($^{129}$I och $^{129}$IO₃⁻) användas för att undersöka spridningen av Medelhavsvattnets utflöde, Mediterranean Outflow Water (MOW). Potentiella tillämpningar av $^{129}$I i marina ekosystem diskuteras även i avhandlingen. Slutligen görs uppskattningar av totala mängden $^{129}$I i Nordsjön och Engelska kanalen där resultaten tyder på att > 90 % av $^{129}$I förekommer i östra Engelska kanalen och södra bukten. Största delen av de $^{129}$I-utsläppen som kommer från La Hague och Sellafield har dock borttransporterat med konvektivet flöde från Engelska kanalen-Nordsjön-systemet och kan därigenom nå Atlantens subtropiska havsströmsområde. För närvarande anses inte $^{129}$I skadligt påverka människors hälsa, men på grund av dess höga mobilitet och långa halveringstid, liksom det faktum att mer än 90 % av allt använt kärnbränsle fortfarande väntar på upparbetning kan en framtid potentiell risk föreligga. Fiskotolit, som uppvisar årsringar och därmed visar på fiskens livslängd och hur den migrerar, har använts som ett intressant miljöarkiv med möjlighet att även återspeglar jod och dess isotope after-
som både $^{127}\text{I}$ och $^{129}\text{I}$ har påträffats i denna vävnad. Därmed kan kunskaper om jodisotoperna $^{129}\text{I}$ och $^{127}\text{I}$ och deras olika kemiska former i havsvatten öppna för en ny intressant metod där tillväxt och migrationsvägar för fiskar kan studeras.
9. References


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