Doctoral Dissertation (Censored)

博士論文 (要約)

# Analysis of carbon dynamics in the Sanriku coastal ecosystem using radiocarbon isotopic compositions

# （放射性炭素同位体比を用いた三陸沿岸生態系の炭素動態の解析）

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# Abstract

The Sanriku coastal region, in the northeast of Honshu, Japan, is a region of mixing between the Oyashio (cold and nutrient-rich aged water mixed with North Pacific Deep Water) and Kuroshio (warm and nutrient-poor water). Seasonal intrusion of the Oyashio enhances primary productivity and may provide an important food resource for organisms in Sanriku. In addition, numerous small enclosed or semi-enclosed bays along the coast of the Sanriku region receive inputs of terrestrial organic matter, which is composed of materials of various ages. Old organic matter might flow into the embayment ecosystem and enter its food web. Recently, radiocarbon ($^{14}C$, with a half-life of 5,730 years) analysis has been used in ecological studies. Measuring the abundance of radiocarbon ($\Delta^{14}C$) provides information regarding age, which is useful for identifying water masses and determining the contributions of old carbon resources to marine environments.

The primary goal of this study was to elucidate the carbon cycle of the Sanriku coastal ecosystem using the radiocarbon technique, with a focus on the benthic food web. In particular, this study focused on four hypotheses: (1) the Oyashio and Kuroshio are major carbon sources in the Sanriku region and can be distinguished by $\Delta^{14}C$; (2) Oyashio-derived carbon can be detected using $\Delta^{14}C$ values of benthic primary producers (macroalgae); (3) Oyashio-derived carbon is a significant carbon source for offshore megabenthos because of its high productivity; (4) aged organic matter is incorporated into benthic consumers at a higher trophic level in the coastal ecosystem.

In chapter 1, I provided an overview on the basic principles of radiocarbon dynamics and

their applications in oceanographic and ecological studies. This chapter also introduced general background and objectives of my study.

In chapter 2, I investigated the spatial-temporal distributions of $\Delta^{14}C$ in dissolved inorganic carbon (DIC) in the Sanriku region and compared these data with oceanographic conditions to confirm their relationship. Surface water samples (depth: 0–200 m) were collected at 13 stations during four cruises conducted between 2014 and 2016, for determination of $\Delta^{14}C$-DIC values. My results revealed that the Sanriku region has two carbon sources that can be distinguished by $\Delta^{14}C$ signatures: warm waters (Kuroshio, Tsugaru, and surface layer waters) with high $\Delta^{14}C$ values (ca. 31‰), and cold waters (Oyashio and cold Oyashio) with low $\Delta^{14}C$ values (ca. –66‰). In addition, my data showed that the $\Delta^{14}C$ values provide information concerning the extent of mixing between warm and cold waters. This study will provide a basis for using $\Delta^{14}C$ as a water mass tracer.

In chapter 3, I explored whether the $\Delta^{14}C$-DIC signals of Oyashio and Kuroshio waters could be detected in primary producers (macroalgae). Cultivation of macroalgae (*Undaria pinnatifida*) was conducted in Otsuchi Bay on the Sanriku coast between November 2013 and April 2014. The $\Delta^{14}C$ values of pinnae (leaflet-like structures, formed in chronological order) at different positions were compared with their $\Delta^{14}C$-DIC values during photosynthesis. During the cultivation period, Oyashio intrusion occurred from early March to early April, accompanied by a reduction in bay water $\Delta^{14}C$-DIC from 15.7 ± 8.6‰ to –57.1 ± 20.7‰. The $\Delta^{14}C$ of the pinnae reflected $\Delta^{14}C$-DIC, as pinnae formed in early March had significantly higher $\Delta^{14}C$ (3.0 ± 5.4‰), compared to pinnae formed in early April (–23.6 ± 7.5‰). These results suggest that the $^{14}C$-depleted signal of the Oyashio is recorded in the

$\Delta^{14}C$ of *U. pinnatifida* pinnae and can be used as an indicator of the relative contribution of Oyashio and Kuroshio in supporting biomass production. These results demonstrate the utility of $\Delta^{14}C$ for examining the dependency of consumers on food containing carbon from different water masses, as macroalgal $\Delta^{14}C$ signatures should be transferred to their consumers.

In chapter 4, I investigated the relative contributions of warm and cold water masses to food provisioning for deep-sea benthic megafauna using $\Delta^{14}C$. I determined the $\Delta^{14}C$ values of benthic invertebrates in seven taxa (three deposit-feeding holothurian species, one suspension-feeding Bivalvia, and three predatory species including Gastropoda and Asteroidea) inhabiting the deep seafloor (depth: 444–2988 m) of two latitudinal transects, the OT line (39°20'N) and ON line (38°25'N). The relative contributions of two water masses to the diets of benthic megafauna were estimated using the isotope mixing model. The estimated contribution of Oyashio-derived carbon to such diets generally exceeded 50%, except for Solasteridae spp. (42%). These results show the relatively large contribution of the Oyashio to the food sources of benthic megafauna, despite the fact that Oyashio generally intrudes into the surface layer in the Sanriku area for only 1–2 months of the year.

Significant differences in $\Delta^{14}C$ were found among taxonomic groups, even along the same latitudinal line. Solasteridae spp. (predator) had a significantly higher $\Delta^{14}C$ level than deposit-feeding sea cucumbers (*Bathyplotes* sp., *Scotoplanes* sp.) on the OT line; *Limopsis belcheri* (suspension feeder) had a significantly lower $\Delta^{14}C$ than deposit-feeding sea cucumbers (*Bathyplotes* sp. and *Parastichopus* sp.) and *Neptunea* spp. (predator) on the ON line. These results indicate differences in the relative contribution of food provisioning from the Oyashio system among taxonomic groups and latitude.

In chapter 5, I investigated the source and age of the organic carbon that supports benthic invertebrate biomass in Otsuchi Bay using $\Delta^{14}C$ as an indicator of age and $\delta^{13}C$ as an indicator of a marine or terrestrial source. I determined the $\Delta^{14}C$ and $\delta^{13}C$ values for benthic invertebrates belonging to 14 taxa (including Maldanidae, other polychaetes, Synaptidae, and Nemertea), and two forms of organic matter (sedimentary organic matter and suspended particulate organic matter) that are potential food sources for benthic invertebrates in the surrounding environment. $\Delta^{14}C$-DIC in the bay water was also analyzed to estimate the possible range of $\Delta^{14}C$ signatures of aquatic primary producers, including phytoplankton and benthic algae.

The $\Delta^{14}C$ values of invertebrates varied in the range of –9.8 to 42‰, and were generally similar to those of DIC (3.2 to 35‰). The $\delta^{13}C$ values of most invertebrate taxa were in the range of –20 to –16‰, corresponding to the typical range of $\delta^{13}C$ values for marine phytoplankton and benthic algae. The $\Delta^{14}C$ values of sedimentary organic matter and suspended particulate organic matter varied much more widely among locations and seasons than among DIC and benthic invertebrates, with ranges of –321 to 30‰ (3046 years before present to modern) and –150 to 4.0‰ (1240 years before present to modern), respectively. The relationships among $\Delta^{14}C$, $\delta^{13}C$, and C/N ratio suggest that sedimentary organic matter is a mixture of modern carbon derived from terrestrial vascular plants and old carbon, presumably derived from sedimentary rocks (kerogen); in contrast, suspended particulate organic matter is a mixture of modern carbon derived from marine phytoplankton and resuspended sediments. Thus, I concluded that benthic invertebrates in this bay assimilate only modern carbon originating from contemporaneous autotrophs, despite the widespread occurrence of old carbon in the suspended particulate organic matter and sedimentary organic matter of Otsuchi Bay.

In chapter 6, I synthesized my results and discussed future research perspectives.

# Contents

# Chapter 1

# General introduction

## 1.1 Radiocarbon principles and application as a biogeochemical tracer

### 1.1.1 Basic principles

Radiocarbon ($^{14}C$) is a naturally occurring radioactive isotope of carbon that is produced in the atmosphere by collision of $^{14}N$ with cosmic rays, in the following reaction:

$$\text{neutron} + {}^{14}N \rightarrow {}^{14}C + \text{proton} \qquad (1.1)$$

While carbon stable isotopes ($^{12}C$, $^{13}C$) are abundant, with atmospheric concentrations of 98.89% and 1.11%, respectively, $^{14}C$ has a considerably lower atmospheric concentration (approximately one per 1 trillion $^{12}C$ atoms).

$^{14}C$ atoms formed in the atmosphere are rapidly oxidized to carbon dioxide ($CO_2$) and incorporated into the global carbon cycle. Atmospheric and oceanic $CO_2$ containing $^{14}C$ is assimilated into organic matter through photosynthesis by primary producers (e.g. terrestrial plants, phytoplankton, and algae). Therefore, the $^{14}C$ content (expressed as $\Delta^{14}C$) of organic matter depends on the initial value in inorganic carbon at the time of fixation. The $\Delta^{14}C$ of organic matter is also influenced by depletion due to radioactive decay, with a half-life of

5730 years after the death of a plant or animal. These characteristics make $^{14}C$ a useful tool for dating in the contexts of archaeology, Earth science, and biogeochemistry (Tuniz et al. 1998; Hua 2009).

Generally, $\Delta^{14}C$ is measured using accelerator mass spectrometry (AMS). AMS was developed in the 1970s and 1980s; this method allows direct counting of $^{14}C$ atoms (Tuniz et al. 1998; Jull and Burr 2006). In most laboratories, the carbon contained in the sample is converted to $CO_2$ and then to graphite during preparation of the target for AMS measurement.

$^{14}C$ measurement was originally introduced as a dating method in the archeological and paleoenvironmental fields (Tuniz et al. 1998; Bayliss 2009). In association with technical improvements and its successful application for determining the carbon age of biogenic materials, which can also be useful in ecological studies, the distribution of $^{14}C$ in the natural environment has been increasingly investigated to clarify the natural sources and dynamics of carbon (McNichol and Aluwihare 2007; Guillemette et al. 2017; Larsen et al. 2018).

In ecological studies, radiocarbon results are generally reported as $\Delta^{14}C$, which is obtained by correcting for isotopic discrimination. Similar to $^{13}C$, $^{14}C$ is subject to isotopic fractionation during natural processes such as photosynthesis, assimilation, and respiration; the $^{14}C$ isotopic ratios measured in a sample reflect this fractionation, as well as radioactive decay (McNichol and Aluwihare 2007). Therefore, each $^{14}C$ isotope ratio is normalized to reflect the value it would have if its $\delta^{13}C$ level were −25‰ (the $\delta^{13}C$ value of the theoretical "1890 wood" standard); the $^{14}C$ isotopic ratios measured in a sample therefore indicate values affected primarily by $^{14}C$ decay (McNichol and Aluwihare 2007).

$\Delta^{14}C$ is expressed in per mille (‰) and ranges from −1000‰ (dead) to 0‰ (radiocarbon content in the atmosphere in 1950) (Caraco et al. 2010). $\Delta^{14}C$ is expressed by the following equations (Stuiver and Polach 1977):

$$\delta^{14}C\ (‰) = (R_{sample}/R_{standard} - 1) \times 1000 \qquad (1.2)$$

$$\Delta^{14}C\ (‰) = \delta^{14}C - 2(\delta^{13}C + 25)\ (1 + \delta^{14}C/1000) \qquad (1.3)$$

where $R_{sample}$ and $R_{standard}$ are the $^{14}C/^{12}C$ ratios of the sample and the National Institute of Standards and Technology oxalic acid standard (HOxII, SRM-4990C), respectively. $R_{standard}$ was corrected for decay from AD 1950 to the measurement year (Stuiver and Polach 1977). $\delta^{13}C$ is derived from the $^{13}C/^{12}C$ ratios of the sample and the standard. In equation 1.3, the magnitude of fractionation between $^{14}C$ and $^{12}C$ is assumed to be approximately double the magnitude of fractionation between $^{13}C$ and $^{12}C$. The $\Delta^{14}C$ value can be converted to years before present (yr BP) based on the decay rate and half-life (5730 years) of $^{14}C$, assuming that the $^{14}C$ level in the atmosphere remained constant in the past (Guillemette et al. 2017).

### 1.1.2 Distribution of radiocarbon in the ocean and its application

In oceanographic studies, $^{14}C$ has been used as a tracer of the oceanic carbon cycle, ocean circulation, and upwelling (Broecker et al. 1995; Levin and Hesshaimer 2000; Key et al. 2004; McNichol and Aluwihare 2007; Santos et al. 2011). The distribution of $\Delta^{14}C$ in dissolved inorganic carbon (DIC) in the world's oceans has been investigated in international projects including the Geochemical Ocean Sections Study (GEOSECS) in the 1970s, the

World Ocean Circulation Experiment (WOCE) in the 1990s, and the ongoing Climate Variability and Predictability Program (CLIVAR).

The $\Delta^{14}$C value in DIC ($\Delta^{14}$C-DIC) of seawater exhibits both vertical and lateral gradients. The subtropical gyres of the North Pacific generally have high $\Delta^{14}$C-DIC values at the surface, due to weak vertical mixing. Conversely, in subpolar gyres, low $\Delta^{14}$C-DIC values are observed as a result of mixing with the oldest deep water (North Pacific Deep Water, with $\Delta^{14}$C-DIC values corresponding to over 2000 years of $^{14}$C age) (McNichol and Aluwihare 2007; McMahon et al. 2013). Upwelling alters surface $\Delta^{14}$C-DIC at the regional and seasonal scales. For example, in the California upwelling region, Santos et al. (2011) observed seasonal variations of $\Delta^{14}$C-DIC in surface water in the range of 8 to 14‰, due to upwelling occurring in spring.

The $^{14}$C content of the surface ocean has been affected by nuclear bomb testing in the atmosphere. A large $^{14}$C pulse was added to the atmosphere as a result of nuclear bomb testing in the 1950s and 1960s, and has since progressively declined. Because of a strong atmosphere-sea gradient and relatively long isotope equilibrium time of approximately 10 years (Broecker and Peng 1974; Graven et al. 2012), bomb-produced $^{14}$C has penetrated the ocean decades later, and surface ocean $^{14}$C continues to decrease (Key et al. 2004; McNichol and Aluwihare 2007; Graven et al. 2012). Tracking bomb $^{14}$C can be useful for understanding oceanic circulation.

GEOSECS data showed that bomb $^{14}$C levels in the equatorial zone, Antarctic zone, and high-latitude North Pacific were lower than the levels in the subtropical and northern North Atlantic. This pattern was explained by the transport of bomb carbon from a region dominated by upwelling to a region dominated by downwelling (Broecker et al. 1985, 1995). Stuiver et al. (1983) calculated replacement times for Pacific, Indian, and Atlantic Ocean deep waters (below 1500 meters) of approximately 510, 250, and 275 years, respectively, based on GEOSECS data from the 1970s. Kumamoto et al. (2002) reported that bomb $^{14}C$ is decreasing in the Oyashio region, but is accumulating in the intermediate waters of the Kuroshio region.

### 1.1.3 Application of $^{14}C$ in aquatic food web studies

Environmental $^{14}C$ signatures provide information regarding potential carbon sources in natural environments, as well as a basis for establishing age. Stable carbon isotope ($\delta^{13}C$) data have been widely used to identify carbon sources for food webs and ecosystems. However, the overlap between the isotope ratios of different carbon sources and spatiotemporal variations in the $\delta^{13}C$ of primary producers impede accurate assessments of carbon dynamics in ecosystems (Middelburg 2014; Marwick et al. 2015). $^{14}C$ is a promising approach to overcome this problem, as it provides information regarding age and can distinguish between ancient and modern carbon sources. The combined use of $\Delta^{14}C$ and $\delta^{13}C$ is especially suitable for tracking old organic carbon in aquatic ecosystems and food webs (Middelburg 2014; Ishikawa et al. 2015; Marwick et al. 2015).

Measurements of natural $^{14}C$ variations have revealed that highly aged ($^{14}C$-depleted) organic matter is ubiquitous in freshwater and coastal ecosystems (Raymond and Bauer 2001a; Goñi et al. 2005; Guillemette et al. 2017). Old organic matter is likely to flow into the aquatic environment from various organic carbon reservoirs through natural processes (e.g., degradation/erosion of unperturbed soil and penetration of hydrocarbons), anthropogenic impacts (e.g., agriculture and urbanization), and as a result of climate change-induced disturbance of long-standing organic carbon reservoirs (e.g., melting of glaciers and thawing of permafrost) (Guillemette et al. 2017).

Furthermore, some studies have used $^{14}C$ to provide evidence supporting the incorporation of ancient allochthonous organic carbon as an essential food source for microbes (Cherrier et al. 1999; McCallister et al. 2004; Singer et al. 2012; Mann et al. 2015; Bellamy and Bauer 2017), zooplankton (Caraco et al. 2010), and invertebrates and higher trophic levels including fish and waterfowl (Schell 1983; Hågvar and Ohlson 2013; Fellman et al. 2015). For example, in glacial ecosystems, ancient carbon is incorporated into microbial and metazoan food webs (Bardgett et al. 2007; Hågvar and Ohlson 2013; Fellman et al. 2015). Such findings suggest that following its assimilation by microbes, glacier-derived organic carbon is consumed and transferred to metazoan biomass. In the Hudson River, Caraco et al. (2010) reported that cladoceran and copepod zooplankton have −240‰ $\Delta^{14}C$ (corresponding to an age of approximately 2200 yr BP), while modern primary production in the river or its watershed is −60 to 50‰ $\Delta^{14}C$, indicating that zooplankton utilize terrestrial soil organic matter of millennial age. McCallister et al. (2004) reported that $\Delta^{14}C$ of bacterial nucleic acids in the Hudson River ranged from −153 to 16‰, indicating a contribution of old terrestrial organic matter derived from soils. In the Hudson River basin, agriculture and other human activities enhance the input of old organic matter (Butman et al. 2015), which may then be assimilated by estuarine organisms.

In contrast, studies in Lake Superior (Zigah et al. 2012; Kruger et al. 2016) and the coastal ocean (DeMaster et al. 2002; Purinton et al. 2008) demonstrated that the $\Delta^{14}C$ characteristics of zooplankton and invertebrates were similar to $\Delta^{14}C$-DIC, rather than $\Delta^{14}C$ of particulate organic matter (POM) or sedimentary organic matter (SOM) in the environment. In these areas, aquatic primary producers, which incorporate DIC as their carbon source, have been presumed to preferentially be used by consumers.

## 1.2 Oceanographic characteristics of the Sanriku region

### 1.2.1 Kuroshio-Oyashio mixing region

The Sanriku coastal region, off the northeast of Honshu, Japan, is known as a mixing region, where waters from two different sources, the Oyashio and Kuroshio, mix in a complex manner (Kawai 1972; Hanawa and Mitsudera 1987). The subtropical gyre originating from the Kuroshio is characterized by high-temperature, high-salinity water. The Kuroshio flows along the southern coast of the Japanese archipelago from the northern Philippines and eastern Taiwan. In the surface layer, the Oyashio is distributed north of the Sanriku area for most of the season, and generally shifts southward in winter via the southern Kuril Islands and southeast coast of Hokkaido, extending to the Sanriku region. The complex water mass structure formed by the Oyashio and Kuroshio has a considerable impact on the carbon cycle and biogeochemical processes in this region (Yatsu et al. 2013).

Despite the importance of Oyashio-derived carbon to biological productivity in the

Sanriku region, the quantitative contribution of Oyashio-derived carbon to Sanriku ecosystems remains unclear. Previous studies have evaluated Oyashio intrusion and the mixing ratio based on salinity and water temperature (e.g., Hanawa and Mitsudera 1987). Other chemical components, such as potential alkalinity (Kakehi et al. 2017), have also been used to estimate the Oyashio mixing ratio. Although these indicators can be used to evaluate the mixing ratio of Oyashio, it is difficult to determine how carbon transported by the Oyashio contributes to the production of consumers at higher trophic levels. In contrast to other indicators, $^{14}C$ can be used to directly estimate the relative contribution of carbon from the Oyashio. Because the water masses of the Oyashio current originate from deeper water layers, they are substantially depleted in $^{14}C$, relative to Kuroshio water masses (Kumamoto et al. 2002; Larsen et al. 2018). Ding et al. (2018) estimated the mixing ratio between the Kuroshio and deep Oyashio by measuring $\Delta^{14}C$-DIC. Based on the definition of $\Delta^{14}C$, phytoplankton (the main primary producers in the coastal region) should have $\Delta^{14}C$ values equivalent to those of DIC. Therefore, utilizing the difference in $\Delta^{14}C$-DIC between Kuroshio and Oyashio waters, the relative contribution of Oyashio-derived carbon can be estimated. However, in order to use this method, examining the current values of $\Delta^{14}C$-DIC in the Oyashio and Kuroshio in the Sanriku region is essential because the $\Delta^{14}C$-DIC in the surface ocean has gradually decreased with decreasing bomb-produced $^{14}C$, resulting in the deviation of current $\Delta^{14}C$-DIC values in surface oceans from those determined in 1970's and 1980's (Key et al. 2004; McNichol and Aluwihare 2007).

### 1.2.2 Oceanographic conditions in small bays

The coastal environment of the Sanriku region is characterized by the presence of numerous small enclosed or semi-enclosed bays. These bays usually occur at river mouths and open to the North Pacific Ocean. The lengths of these bays range from several to a few tens of kilometers. Oceanographic conditions in the bays are influenced by freshwater inputs from rivers and intrusion of various currents. During most seasons, the Tsugaru warm current (a branch of the Kuroshio) flows out to the Pacific through the Sea of Japan and Tsugaru Strait, then intrudes into the bays; furthermore, the Oyashio occasionally influences bay waters in winter (Fukuda et al. 2016; Ishizu et al. 2017).

Terrestrial inputs from land and autochthonous production (i.e., marine phytoplankton, seaweed, and benthic algae) are essential sources of organic matter in the estuary and bays (Goni et al. 1997; Hedges et al. 1997; Raymond and Bauer 2001a; Ogrinc et al. 2005). High biological productivity is common in coastal areas, driven by terrestrial- and marine-origin nutrient supplies, anthropogenic inputs, and complex hydrodynamics (Smith and Hollibaugh 1993; Antonio et al. 2010; Cai 2011; Bianchi et al. 2018). Terrestrial organic matter is supplied to coastal bays by rivers and wind (Schlünz and Schneider 2000). Organic matter discharged from land to the sea is typically found along a gradient from the river mouth to the head of the bay (Little 2000). Consequently, the contributions of terrestrial resources to the food sources of some benthic invertebrates vary spatially (Doi et al. 2005; Kasai and Nakata 2005; Sakamaki et al. 2010). Previous studies of the distribution of allochthonous matter in bays in the Sanriku region are scarce, but Wada et al. (1987) reported that sediments in Otsuchi Bay were primarily composed of terrestrial organic matter. Lu et al. (2016)

investigated lignin phenols, which are derived from terrestrial plants, in Otsuchi Bay; they demonstrated the substantial removal of lignin phenols by microbial degradation in bay waters. The hydrographic conditions of the bay differ markedly from those of the offshore area (Ishizu et al. 2017), leading to the establishment of different carbon cycles in the coastal ocean and the bay.

Aged materials are generally assumed to provide minimal contributions to aquatic food webs, in comparison to modern sources (Bellamy and Bauer 2017). Contrary to this paradigm, recent studies have suggested that aged carbon is assimilated into aquatic food webs as readily as newly produced organic matter with a modern carbon age (Bellamy and Bauer 2017). For example, aged organic matter from soils that is transported to estuarine and coastal environments can be assimilated by microbes (McCallister et al. 2004). Such findings suggest that aged organic carbon might support the production of benthic invertebrates in coastal habitats via the microbial food chain. However, prior studies primarily focused on organisms at lower trophic levels, such as microbes, and on freshwater ecosystems. The contribution of aged carbon to consumer biomass has also been examined in inland macroinvertebrates and fishes (e.g., Schell 1983; Hågvar and Ohlson 2013), but rarely in coastal areas.

## 1.3 Objectives

The primary goal of this study was to elucidate the carbon cycle of the Sanriku coastal ecosystem using a radiocarbon technique, with a focus on macroalgae and benthic invertebrates. Figure 1.1 shows a schematic diagram of the carbon pathway in marine ecosystems. DIC is incorporated into primary producers (i.e., phytoplankton, algae, and seaweeds) as a substrate for photosynthesis. Primary producers are the starting point of the food web, providing organic carbon to consumers at higher trophic levels. Photosynthesis in surface waters supplies the majority of organic carbon to the ocean and provides an important food resource for deep-sea benthic consumers through the sinking of particles. In addition to this pathway, aged carbon from terrestrial ecosystems is a potential carbon source for benthic consumers in coastal bays. Within this pathway, it is possible to distinguish and evaluate the contributions of carbon derived from multiple sources (i.e., Oyashio vs. Kuroshio origin, aged vs. modern) by comparing $\Delta^{14}$C values at each step: DIC, primary producers, and benthic consumers.

Therefore, to clarify the carbon pathway in the Sanriku region, the following four hypotheses were examined.

(1) The Oyashio and Kuroshio are major carbon sources in the Sanriku region and can be distinguished by $\Delta^{14}$C.
(2) Oyashio-derived carbon can be detected using $\Delta^{14}$C values of benthic primary producers (macroalgae).
(3) The Oyashio is a significant carbon source for offshore megabenthos because of its high productivity.
(4) Aged organic matter is incorporated into benthic consumers at a higher trophic level in the coastal ecosystem.

In chapter 2, I investigated the spatio-temporal distributions of $\Delta^{14}$C-DIC in the Sanriku region to evaluate the relationship between oceanographic conditions and $\Delta^{14}$C-DIC (hypothesis 1). I also aimed to determine whether the $\Delta^{14}$C-DIC observed in the region exhibited sufficient dynamic range for identification of source contributions in the following chapters.

In chapter 3, $\Delta^{14}$C of the large brown macroalga *Undaria pinnatifida* was investigated as an indicator of oceanographic conditions during algal growth, using a cultivation experiment (hypothesis 2). The $\Delta^{14}$C values of *U. pinnatifida* pinnae reflect $\Delta^{14}$C-DIC values in bay water during algal growth. Because of the annual life cycle and rapid winter growth of *U. pinnatifida*, their pinnae could serve as a record of Oyashio intrusion into the bay.

In chapter 4, I investigated the relative contributions of warm and cold water masses to the provisioning of organic carbon assimilated by benthic megafauna, through measurements of the $\Delta^{14}$C values of benthic invertebrates, including various taxa inhabiting the deep seafloor at two latitudes (hypothesis 3). Differences among species and among functional groups with different feeding strategies were also examined.

In chapter 5, I investigated the source and age of organic carbon supporting benthic invertebrate biomass in Otsuchi Bay through the combined use of $\Delta^{14}$C and $\delta^{13}$C values (hypothesis 3). I determined the $\Delta^{14}$C and $\delta^{13}$C values of benthic invertebrates in various taxa, as well as two forms of organic matter in the surrounding environment (i.e., SOM and POM), which are potential food sources for benthic invertebrates.

In chapter 6, I synthesize these results and discuss future research perspectives.

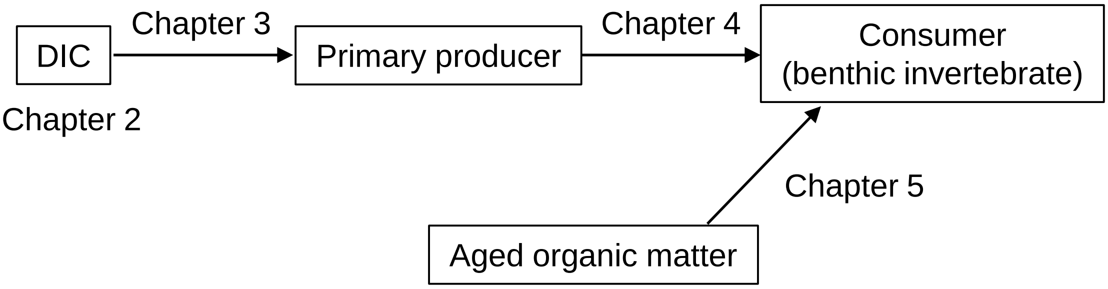

Fig. 1.1. A schematic diagram of the carbon pathways in coastal marine ecosystems. This thesis focuses on the $\Delta^{14}C$ variabilities associated with the DIC pool (chapter 2), those with the carbon flow from DIC to primary producer (macroalgae) (chapter 3), those with the coupling between surface primary production and deep sea benthic megafauna (chapter 4), and those with the consumption of aged organic matter by benthic invertebrates (chapter 5).

# Chapter 2

## Spatial-temporal distribution of $\Delta^{14}$C-DIC in the Sanriku region

本章については、5年以内に雑誌等で刊行予定のため、非公開。

## Chapter 3

# Position-dependent radiocarbon content of the macroalgae *Undaria pinnatifida* as an indicator of oceanographic conditions during algal growth

## 3.1 Introduction

The $\Delta^{14}$C-DIC in surface seawater is influenced by upwelling because there is less $^{14}$C in deeper water than in surface water (Key 2001). For example, in the coastal upwelling region of California, there was a decrease in $\Delta^{14}$C-DIC from 42 to 26‰ during active upwelling in 2006 (Santos et al. 2011). $\Delta^{14}$C signals during upwelling are transferred to biogenic carbonates present in hard tissues such as bivalve shells, thus providing a temporal record of the strength of upwelling (Douka et al. 2010; Santos et al. 2011; Ferguson et al. 2013). Because DIC is fixed by photosynthesis, the soft tissues of primary producers such as macroalgae might also reflect the $\Delta^{14}$C-DIC of upwelled waters and serve as an indicator of oceanic conditions during their growth. Such information could be useful for assessing the influence of oceanic conditions (upwelling strength and current regimes) on macroalgal growth and distribution. However, to the best of my knowledge, no previous studies have examined whether the $\Delta^{14}$C of macroalgal tissues record changes in $\Delta^{14}$C-DIC in the surrounding seawater during their growth.

In this study, I examined the $\Delta^{14}$C of the large brown macroalga *Undaria pinnatifida* (Laminariales) growing in an embayment of Otsuchi Bay on the Sanriku coast of northeastern Japan (Fig. 3.1a). *Undaria pinnatifida* is extensively cultivated in this region, and previous studies have examined the nutrient sources, photosynthetic rates, and other physiological parameters of this kelp species (e.g., Yoshikawa et al. 2001; Carvalho et al. 2009; Gao et al. 2013b; Endo et al. 2017, 2018). The current system comprises the Kuroshio subtropical western boundary current, the Tsugaru Warm Current, and the subarctic cold Oyashio Current (Hanawa and Mitsudera 1987; Shimizu et al. 2001; Oguma et al. 2002; Ishizu et al. 2017). Because the Oyashio Current originates from high latitudes of the North Pacific, where $^{14}$C-depleted deep water is upwelled, Oyashio waters have substantially less $^{14}$C ($\Delta^{14}$C-DIC: –60 to –10‰) than the Tsugaru Warm Current waters and Kuroshio waters ($\Delta^{14}$C-DIC: 20–40‰); in the latter, $\Delta^{14}$C-DIC is strongly influenced by the uptake of $^{14}$C derived from atmospheric nuclear bomb testing in the 1970s (Key 2001; Kumamoto et al. 2002; Key et al. 2004; Ge et al. 2016; see chapter 2). *Undaria pinatifida* sporophytes grow rapidly in winter (Yoshikawa et al. 2001), when the prevailing oceanic current changes from the warm current to the Oyashio Current (Ishizu et al. 2017). New pinnae (leaflet-like structures) on sporophytes are synthesized near the meristem, which is located near the bottom of the thallus (Fig. 3.2). As the thallus grows, it expands upwards and a pair of new pinnae form below the older ones. Thus, the positions of pinnae along the major axis of the thallus represent the pinna formation chronology.

In this study, I tested the hypothesis that the $\Delta^{14}$C of *U. pinnatifida* pinnae reflects the $\Delta^{14}$C-DIC in bay water during photosynthetic production by each pinna. To test this hypothesis, *U. pinnatifida* seedlings were outplanted in Otsuchi Bay, and the $\Delta^{14}$C variability at different pinna positions was examined in relation to temporal changes in bay water salinity, temperature, and $\Delta^{14}$C-DIC levels.

## 3.2 Materials and Methods

### 3.2.1 Study site

*Undaria pinnatifida* cultivation was conducted in Otsuchi Bay (length: 8 km, width: 2–4 km, depth 9–60 m), a semi-closed bay open to the northwest Pacific Ocean. Oceanic conditions in the bay are related to the coastal ocean outside of the bay due to rapid water exchange between the bay and open ocean (Otobe et al. 2009; Ishizu et al. 2017; Tanaka et al. 2017). Between October and February, the bay water is generally under the influence of the Tsugaru Warm Current, and the intrusion of Oyashio water occurs between February and April (Ishizu et al. 2017; Tanaka et al. 2017). Three rivers (the Otsuchi, Koduchi, and Unozumai) flow into the bay with a total discharge of 3–35 $m^3 s^{-1}$ (Anbo et al. 2005).

### 3.2.2 Outplanting and sampling of *U. pinnatifida*

Sporophyte seedlings were obtained from a local fisherman (the general method used for the preparation of sporophyte seedlings was described in Endo et al. 2017) and were outplanted on November 21, 2013, at three stations in Otsuchi Bay (Fig. 3.1a). At each station, sporophytes (>2 cm) were attached to a seeded string that was wrapped around a vertical cultivation rope and suspended at a depth of 1–3 m (Yoshikawa et al. 2001). A temperature–

salinity logger (Infinity-CTW; JFE Advantech Co, Ltd., Japan) was attached to the line at a depth of approximately 3 m to collect seawater temperature and salinity data every 10 min. On March 3, 2014, a hole (diameter: 5 mm) was punched into the thallus near the meristematic region as a marker of sporophyte growth (Mann 1973; Yoshikwawa et al. 2001; Fig. 3.2b). *Undaria pinnatifida* individuals (thallus length: 105–175 cm) were harvested on April 8, 2014 (138 days after outplanting) at Stations (Sts.) A2 (n = 2), A3 (n = 3), and A7 (n = 3) (individual codes are listed in Table 3.1). I conducted transect sampling for $\Delta^{14}$C analyses in four haphazardly selected individuals (S1, 3, 4, and 6), on 13–20 pinnae positioned between the hole (upper pinnae) and meristem (lower pinnae) (Fig. 3.2). In four additional individuals (S2, 5, 7, 8), I conducted two-point sampling, removing only pinnae positioned near the punch hole and near the meristem. Sampling was conducted by removing the top 5 cm of the pinnae (width: ca. 2 cm, length: 5–30 cm) using scissors.

Pinna position (cm) was defined as the distance from the hole to the base of pinna after normalization to correct for differences in blade length among individuals (Fig. 3.2b). Normalization was conducted according to the following equation:

$$L_a = \frac{L_1}{L_1 + L_2} \times M, \qquad (3.1)$$

where $L_1$ is the distance (cm) between the punch hole and the base of pinna A, $L_2$ is the distance (cm) between the meristem and the base of pinna A, and the $M$ is the average value of $L_1 + L_2$ for four individuals (mean and standard deviation: 66.2 ± 8.6 cm).

### 3.2.3 Seawater and river water sampling to determine DIC concentration and $\Delta^{14}$C-DIC

Seawater samples were collected in Otsuchi Bay at depths of 1 and 3 m on January 21, March 3, and April 8, 2014. River water samples were collected at the mouths of the Otsuchi, Koduchi, and Unozumai rivers where they flowed into the bay (Fig. 3.1a), on January 22, March 3, and April 12, 2014. To examine water mass distribution along the Snariku coast during the study period, I also collected offshore water using the R/V Shinsei-Maru on March 16 and 18, 2014, along transects from river mouths to offshore of Otsuchi Bay (Sts. 2, OT3–6) and offshore of Onagawa Bay (south of Otsuchi Bay, ON7 and ON8) (Fig. 3.1b). Samples were collected from one to six depths at each station.

River water samples were collected using a plastic bucket and stored in 500 mL glass bottles with plastic caps. Seawater (bay and offshore) samples were collected using 12 or 5 L Niskin bottles, except that a plastic bucket was used to collect surface water. Seawater samples were stored in 100 mL glass vials with rubber stoppers. River and seawater samples were preserved with $HgCl_2$; saturated aqueous solution of $HgCl_2$ was added to the sample at a volumetric ratio ($HgCl_2$ : sample) of 1:1,000.

### 3.2.4 Chemical analysis

Macroalgal samples were acidified overnight by fumigating with HCl in centrifugation tubes to remove inorganic carbon. After removing excess HCl using a vacuum desiccator, dried samples were combusted in evacuated quartz tubes containing copper oxide and Sulfix for 30 min at 500°C, followed by oxidation to $CO_2$ for 2 h at 850°C. Then $CO_2$ was purified in a vacuum line for graphitization (Yokoyama et al. 2007). The DIC in seawater (230 mL) or river water (570 mL) samples were extracted as $CO_2$ gas and graphitized using the vacuum line following the procedure described in chapter 2. The DIC concentrations of seawater and river water were calculated from the pressure of $CO_2$ gas extracted from the vacuum line for the graphitization (McNichol et al. 1994). $\Delta^{14}C$ of the graphite sample was analyzed by the SSAMS (National Electrostatics Corporation, USA). Detailed information for the $\Delta^{14}C$ measurements is provided in chapter 2.

### 3.2.5 Statistical analysis

Statistical analyses of $\Delta^{14}C$ data were conducted using Student's *t* test or two-way analysis of variance (ANOVA) at a level of $p < 0.05$ after confirming that the data met the normality (Shapiro–Wilk test) and equal variance (Bartlett test) assumptions. When these assumptions were not fulfilled, nonparametric tests (the Kruskal–Wallis test followed by the Steel–Dwass multiple comparison test or Spearman's rank correlation analysis) were conducted. All statistical analyses were performed using R v.3.3.2 (R Development Core Team 2016).

## 3.3 Results

### 3.3.1 Temporal variation in salinity and temperature in the bay

In Otsuchi Bay, seawater temperature gradually decreased from late November (15°C) to early March (6.7°C) (Fig. 3.3a). At Sts. A2 and A3, salinity did not significantly change between November 22 and March 5, with an average value of 33.5 ± 0.13. Salinity markedly decreased from March 6 to early April, accompanied by a decrease in temperature (Fig. 3.3b). At St. A7, general trends in seasonal salinity and temperature were similar to those at other stations, except for the presence of short-term (timescale of a few days) fluctuations in salinity and temperature (Fig. 3.3a, b). Both temperature and salinity were generally lower at St. A7 than at Sts. A2 and A3 (Fig. 3.3a, b).

### 3.3.2 $\Delta^{14}$C-DIC and DIC concentrations in bay and river water

In bay water, the mean $\Delta^{14}$C-DIC values were 17.5‰ ± 6.1‰ and 15.7‰ ± 8.6‰ on January 21 and March 3, respectively, and differences between the values obtained for those dates were not significant ($p > 0.05$) (Table 3.2). The mean $\Delta^{14}$C-DIC of seawater on April 8 (–57.1‰ ± 20.7‰) was significantly lower than the corresponding values on January 21 and March 3 ($p < 0.05$, Table 3.2). The $\Delta^{14}$C-DIC offset between March 3 and April 8 was 72.8‰. The DIC concentration in bay water was in the range 1.82–2.12 mM, changing little over time (Table 3.2). The $\Delta^{14}$C-DIC and DIC concentrations in river water ranged from –35.3 to 8.9‰ and from 0.33 to 0.53 mM, respectively (Table 3.3).

### 3.3.3 Temperature, salinity, and $\Delta^{14}$C-DIC in offshore waters

In seawater off Otsuchi Bay (Sts. 2, OT3–5), a cold (1.5–4.1°C) and low-saline (32.7–33.5) water mass prevailed at depths of 0–200 m. Warmer (7.0–8.1°C) and saltier (33.5–33.7) waters were prevalent in the region approximately 60 km south of the OT stations (off Onagawa Bay, Sts. ON7–8; Fig. 4a, b, Table 3.4). Values of $\Delta^{14}$C-DIC in the upper water column (depth: 0–200 m) of the OT stations ranged from –73.7 to –7.6‰, whereas corresponding values for seawater collected at ON stations were higher, ranging from –9.6 to 8.1‰ (Fig. 3.4c, Table 3.4). The $\Delta^{14}$C-DIC values of seawater collected at a depth of 1000 m ranged from –199 to –192‰ (Table 3.4).

### 3.3.4 $\Delta^{14}$C of *U. pinnatifida* pinnae

Data collected using the transect and two-point sampling methods were used to obtain mean $\Delta^{14}$C values for upper (old) and lower (young) *U. pinnatifida* pinnae. Depending on the station, mean $\Delta^{14}$C values of the upper and lower pinnae ranged from 1.2 to 5.9‰ and from –25.4 to –21.2‰, respectively (Table 3.5). To examine the significance of the differences in $\Delta^{14}$C values among stations and between positions, two-way ANOVA was conducted using station and position as two fixed factors. The results showed that $\Delta^{14}$C values differed significantly ($p < 0.05$) between positions (upper versus lower pinnae), whereas the difference among stations (A2, A3, and A7) was not significant ($p > 0.05$). For the pooled data, the mean $\Delta^{14}$C of the upper pinnae (mean ± SD: 3.0 ± 5.4‰) was significantly lower than that of the lower pinnae (–23.6 ± 7.5‰), with an offset value of 26.6‰ ($p < 0.0001$, Student's *t* test) (Table 3.5, Fig. 3.5).

The results of pinna transect sampling revealed a decreasing trend in $\Delta^{14}$C from the upper (near the punch hole) to the lower (near the meristem) pinnae (Fig. 3.6). The correlation between pinna position and $\Delta^{14}$C was significant for four individuals ($r_s = -0.579$ to $-0.863$, $p < 0.05$) and the pooled data ($r_s = -0.619$, $p < 0.001$) (Table 3.6).

## 3.4 Discussion

The most important finding of this study is that the $\Delta^{14}$C of pinnae displayed systematic position-dependent variability, with an offset of 26.6‰ between pinnae formed in early March and those formed in early April. I argue that this $\Delta^{14}$C shift in *U. pinnatifida* pinnae tissues reflected changes in oceanic current conditions in the bay.

### 3.4.1 Oyashio intrusion and $\Delta^{14}$C-DIC

The decreasing trend in salinity and temperature in the bay between March 6 and April 8 was primarily a consequence of the Oyashio intrusion during this period. This assertion is supported by the results of Ishizu et al. (2017) from a time series of mooring and hydrographic observations at the mouth of Otsuchi Bay; a prominent low-salinity event occurred between early March and April, 2014. Satellite imagery showed that cold Oyashio water gradually moved north to south to cover the Sanriku coast north of 39°N in early March, including the area outside of Otsuchi Bay (Ishizu et al. 2017). These results indicate that the low-salinity event was caused by the intrusion of Oyashio water from offshore. Although marked decreases in both salinity and temperature were observed in the current study after March 6 at the three stations, salinity was generally low at St. A7 (south of the bay), with short-term large-amplitude fluctuations. The river plume was directed southward due to the Coriolis force in the Otsuchi Bay, and low-salinity fluctuations at St. A7 appear to have been caused by river discharge (Ishizu et al. 2017).

The substantial decrease in $\Delta^{14}$C-DIC from 16.6‰ (January 21 and March 3) to –57.1‰ (April 8) in the bay can be explained by the gradual mixing of $^{14}$C-rich seawater of subtropical origin with $^{14}$C-depleted Oyashio water. Consistent with this notion, my data collected at OT stations during mid-March showed that the $^{14}$C-depleted water mass ($\Delta^{14}$C-DIC: –73.7 to –7.6‰) was indeed prevalent in the surface layer (0–200 m depth) near the mouth of the bay (Fig. 3.4, Table 3.4). This water mass was characterized by low temperature (1.5–4.1°C) and low salinity (32.7–33.3) indicative of Oyashio or Oyashio-influenced coastal Oyashio water according to the Sanriku water mass classification proposed by Hanawa and Mitsudera (1987), and therefore may have been a source of the $^{14}$C-depleted water that intruded into the bay (see chapter 2). Values of $\Delta^{14}$C-DIC were higher at ON stations than at OT stations, suggesting that $^{14}$C-depleted waters moved from north to south as the Oyashio gradually moved southward after early March in areas offshore the Sanriku coast. The presence of $^{14}$C-depleted deep water (depth: 1000 m) with an estimated radiocarbon age of ca. 2000 years in this region is consistent with the results of previous studies (see McNichol and Aluwihare 2007).

In addition to Oyashio intrusion, the river discharge might have decreased the salinity of the bay water, thereby causing $^{14}$C depletion of bay water (hard water effect, Philippsen 2013).

In fact, my data showed that the river DIC was generally depleted in $^{14}$C (the lowest $\Delta^{14}$C-DIC value of –35.3‰ was observed on March 3 at the Koduchi River; Table 3.3). To evaluate the maximum potential influence of the river discharge on the $\Delta^{14}$C-DIC value of bay water, I constructed the following simple two-end-member mass balance model, assuming that the decrease in salinity from March 3 ($\mathrm{Sal_1}$, range 32.3–33.4, Fig. 3.3) to April 8 ($\mathrm{Sal_2}$, range 31.8–32.4, Fig. 3.3) was caused solely by river discharge into the bay:

$$\Delta^{14}\text{C-}\,\mathrm{DIC_{mix}} = \frac{f\,[\mathrm{DIC_r}]\,\Delta^{14}\text{C-}\mathrm{DIC_r} + (1-f)\,[\mathrm{DIC_1}]\,\Delta^{14}\text{C-}\mathrm{DIC_1}}{[\mathrm{DIC_{mix}}]}, \qquad (3.2)$$

In this model, $f$ is the maximum potential fraction of river water in the bay water samples collected on April 8, which was calculated using the following equation: $f = (\mathrm{Sal_1} - \mathrm{Sal_2})/(\mathrm{Sal_1})$ (estimated range of $f$: 0.016–0.034). $[\mathrm{DIC_r}]$ and $\Delta^{14}\text{C-}\mathrm{DIC_r}$ represent the DIC concentration and $\Delta^{14}$C-DIC of river water, respectively [to determine these parameters, the maximum DIC concentration of 0.53 mM (Table 3.3) and the lowest $\Delta^{14}$C-DIC value of –35.3‰ (Table 3.3) were used to evaluate the maximum influence of river water on $\Delta^{14}$C-DIC in the bay]. $[\mathrm{DIC_1}]$ and $\Delta^{14}\text{C-}\mathrm{DIC_1}$ represent the DIC concentration and $\Delta^{14}$C-DIC of bay water collected on 3 March, respectively (these parameters were set to 1.92 mM and 15.7‰, respectively, based on the data presented in Table 3.2). $[\mathrm{DIC_{mix}}]$ and $\Delta^{14}\text{C-}\mathrm{DIC_{mix}}$ are the estimated DIC concentration and the estimated $\Delta^{14}$C-DIC value, respectively, of "virtual" water obtained by mixing the bay water collected on March 3 with river water at a mixing ratio of $f$ ($[\mathrm{DIC_{mix}}] = f[\mathrm{DIC_r}] + (1 - f)[\mathrm{DIC_1}]$). I estimated that $\Delta^{14}\text{C-}\mathrm{DIC_{mix}}$ is in the range 15.2–15.5‰, with an offset value relative to $\Delta^{14}\text{C-}\mathrm{DIC_1}$ of 0.2–0.5‰. This offset value is much smaller than the $\Delta^{14}$C-DIC offset observed in the bay (72.8‰). As the model described above assumed that the decrease in salinity was solely caused by river discharge (thus providing the maximum potential influence of river water on DIC dynamics in the bay), I conclude that river discharge had little effect on temporal variability in bay water $\Delta^{14}$C-DIC.

### 3.4.2 Oyashio intrusion and $\Delta^{14}$C of *U. pinnatifida*

*Undaria pinnatifida* pinnae displayed systematic position-dependent variability in $\Delta^{14}$C, with a tendency for $^{14}$C depletion from older to newly formed pinnae. The most likely explanation for this tendency is a shift in the prevailing current from the warm current to the cold Oyashio Current during *U. pinnatifida* growth. On March 3, bay water DIC was relatively enriched in $^{14}$C, such that the $\Delta^{14}$C of upper pinnae was relatively high. As the Oyashio intrusion progressed, bay water DIC became depleted in $^{14}$C, leading to a decrease in $\Delta^{14}$C in the lower pinnae, which were produced in early April. Thus, the $\Delta^{14}$C distribution in the pinnae recorded the $\Delta^{14}$C shift of ambient DIC associated with changes in the prevailing ocean current.

The $\Delta^{14}$C values of macroalgal photosynthates directly reflect the source $\Delta^{14}$C-DIC signature because $\Delta^{14}$C, by definition, is corrected for isotope fractionation during carbon assimilation and other metabolic processes using the $\delta^{13}$C value (Stuiver and Polach 1977; McNichol and Aluwihare 2007; see chapter 1). Therefore, the effects of isotope fractionation can be ignored in the interpretation of $\Delta^{14}$C variability in and among organisms. However, $\Delta^{14}$C variability among *U. pinnatifida* pinnae should be interpreted with caution because of potential mixing of “old” and “new” photosynthates through metabolic processes. In this study, mean $\Delta^{14}C$ values in upper pinnae (3.0 ± 5.4‰) were lower than the $\Delta^{14}C$-DIC value on March 3 (15.7 ± 8.6‰), and those in lower pinnae (–23.6 ± 7.5‰) were higher than the $\Delta^{14}C$-DIC value on April 8 (–57.1 ± 20.7‰) (Fig. 3.5). Thus, differences in $\Delta^{14}C$ values before and after the Oyashio intrusion were greater for DIC than for pinnae. Deviation of the mean $\Delta^{14}C$ values of pinnae from the corresponding $\Delta^{14}C$-DIC values and apparent attenuation of the isotopic offset for pinnae relative to DIC could be explained by carbon turnover (Carballeira et al. 2014). Pinnae formed in the warm current (high $\Delta^{14}C$) were later exposed to the cold current (low $\Delta^{14}C$), which may have resulted in the mixing of preexisting carbon (high $\Delta^{14}C$) and newly formed carbon (low $\Delta^{14}C$) within a single pinna. Although carbon that is newly fixed by older pinnae is translocated to the meristem to support the formation of younger pinnae (Wu and Meng 1997), the mixing of old and new carbon can still occur due to tissue carbon turnover. For a quantitative assessment of the contributions of different currents to the supply of DIC for pinnae synthesis, the effect of carbon turnover on the $\Delta^{14}C$ signature of pinnae must be evaluated in future research.

It is also important to consider the timescale of blade growth. *Undaria pinnatifida* pinnae elongate from the base (Nishikawa 1974). Previous studies conducted in Otsuchi Bay reported elongation rates of the *U. pinnatifida* thallus on the order of 1–3 cm/day in March (Saitoh et al. 1999; Yoshikawa et al. 2001). Using this elongation rate, the time required for the formation of the top 5 cm of the pinna (the part examined in this study) is estimated to be on the order of 2–5 days. Therefore, the $\Delta^{14}C$ of each matured pinna may reflect the $\Delta^{14}C$-DIC of ambient water integrated over a period of 2–5 days. This time integration of the isotopic signature may contribute to the attenuation (smoothing) of isotopic variability in *U. pinnatifida* relative to the corresponding variability in $\Delta^{14}$C-DIC.

## 3.5 Conclusion

I demonstrated that $\Delta^{14}$C in *U. pinnatifida* pinnae reflected a shift in exposure from a warm current to the cold Oyashio Current during algal growth. Despite the potential influence of tissue turnover, my data clearly show systematic position-dependent variability in $\Delta^{14}$C in *U. pinnatifida*. The large body size and rapid growth of *U. pinnatifida*, which produces a pair of pinnae every 1 or 2 days (Saitoh et al. 1999; Yoshikawa et al. 2001; Gao et al. 2013a), allow us to use its position-dependent variability in $\Delta^{14}$C as a unique tool to reconstruct oceanographic conditions experienced by macroalgae during growth. In addition, the position dependent variability in $\Delta^{14}$C could be used to assess the role of Kuroshio system and Oyashio system in sustaining the biomass production of macroalgae in Sanriku bays. This possibility should be investigated in the future study. As macroalgal $\Delta^{14}$C signatures should transfer to consumers, the $\Delta^{14}$C of consumers could be helpful for examining the dependency of the food web on carbon from different ocean current systems. In chapter 4, I will explore the use of the $\Delta^{14}$C approach in determining the dependency of benthic food web on carbon from Kuroshio and Oyashio systems.

Table 3.1. Summary of codes for the individual *Undaria pinnatifida* samples, sampling stations, and sampling methods.

| Individual code | Station | Sampling method |
|---|---|---|
| S1 | A2 | Transect |
| S2 | A2 | Two-point |
| S3 | A3 | Transect |
| S4 | A3 | Transect |
| S5 | A3 | Two-point |
| S6 | A7 | Transect |
| S7 | A7 | Two-point |
| S8 | A7 | Two-point |

Table 3.2. $\Delta^{14}$C-DIC and DIC concentration in bay water. Letters appended to mean $\Delta^{14}$C-DIC values indicate significant differences between sampling dates ($p < 0.05$, Kruskal–Wallis test followed by Steel–Dwass test). SD: standard deviation.

| Date | Station | Depth (m) | Temp. (°C) | Salinity | $\Delta^{14}$C (‰) | Error (1σ) | DIC concentration (mM) |
|---|---|---|---|---|---|---|---|
| 21 Jan 2014 | A2 | 1 | 9.10 | 32.78 | 23.2 | ±2.8 | 1.82 |
| | | 3 | 9.60 | 33.66 | 19.1 | ±3.6 | 2.04 |
| | A3 | 1 | 9.64 | 33.42 | 22.5 | ±3.9 | 1.84 |
| | | 3 | 9.63 | 33.63 | 5.7 | ±3.5 | 1.96 |
| | A7 | 1 | 8.48 | 32.49 | 13.7 | ±3.7 | 2.06 |
| | | 3 | 8.97 | 32.99 | 20.5 | ±3.0 | 2.12 |
| | mean ± SD | | 9.23 ± 0.47 | 33.16 ± 0.48 | 17.5 ± 6.1 a | | 1.97 ± 0.12 |
| 3 Mar 2014 | A2 | 1 | 5.56 | 31.32 | 2.6 | ±3.7 | - |
| | | 3 | 6.60 | 33.30 | 14.0 | ±3.5 | 1.96 |
| | A3 | 1 | 6.84 | 32.16 | 11.4 | ±3.9 | 1.87 |
| | | 3 | 6.91 | 33.24 | 16.6 | ±3.4 | 1.94 |
| | A7 | 1 | 6.51 | 31.97 | 22.9 | ±3.4 | 1.93 |
| | | 3 | 6.79 | 32.69 | 26.8 | ±3.3 | 1.89 |
| | mean ± SD | | 6.53 ± 0.50 | 32.45 ± 0.77 | 15.7 ± 8.6 a | | 1.92 ± 0.03 |
| 8 Apr 2014 | A2 | 1 | 3.93 | 31.46 | -30.4 | ±3.8 | 1.95 |
| | | 3 | 3.33 | 32.33 | -57.2 | ±3.4 | 1.93 |
| | A3 | 1 | 4.08 | 31.48 | -75.9 | ±3.2 | 1.85 |
| | | 3 | 3.75 | 32.25 | -85.2 | ±3.0 | 2.01 |
| | A7 | 1 | 4.56 | 27.88 | -40.3 | ±3.8 | 1.96 |
| | | 3 | 3.88 | 32.13 | -53.9 | ±3.3 | 1.97 |
| | mean ± SD | | 3.92 ± 0.40 | 31.26 ± 1.70 | -57.1 ± 20.7 b | | 1.94 ± 0.05 |

Table 3.3. $\Delta^{14}$C-DIC and DIC concentration in river water. Errors for $\Delta^{14}$C indicate analytical precision (1σ).

| River | Date | $\Delta^{14}$C-DIC (‰) | DIC concentration (mM) |
|---|---|---|---|
| Otsuchi | 22 Jan 2014 | -10.1 ±2.9 | 0.53 |
| | 3 Mar 2014 | -18.0 ±2.9 | 0.50 |
| | 12 Apr 2014 | -21.8 ±2.9 | 0.45 |
| Koduchi | 22 Jan 2014 | -3.1 ±2.9 | 0.42 |
| | 3 Mar 2014 | -35.3 ±3.0 | 0.40 |
| | 12 Apr 2014 | -2.8 ±4.0 | 0.33 |
| Unozumai | 22 Jan 2014 | 1.3 ±3.0 | 0.44 |
| | 3 Mar 2014 | 8.9 ±2.9 | 0.47 |
| | 12 Apr 2014 | 1.4 ±4.1 | 0.41 |

Table 3.4. Temperature, salinity, denthity and $\Delta^{14}$C-DIC in the offshore region (see Fig. 3.1b for sampling locations). Errors for $\Delta^{14}$C indicate analytical precision (1σ).

| Station | Date | Depth (m) | Temp. (°C) | Salinity | $\sigma_t$ | $\Delta^{14}$C (‰) |
|---|---|---|---|---|---|---|
| St. 2 | 18 Mar 2014 | 0 | 4.10 | 32.70 | 25.95 | -7.6 ±3.2 |
| OT3 | 16 Mar 2014 | 20 | 3.02 | 32.86 | 26.18 | -22.0 ±3.9 |
| | | 66 | 4.01 | 33.08 | 26.26 | -10.0 ±3.3 |
| OT4 | 17 Mar 2014 | 0 | 2.08 | 32.75 | 26.16 | -36.5 ±5.2 |
| | | 20 | 2.10 | 32.77 | 26.17 | -27.9 ±5.7 |
| | | 50 | 2.30 | 32.88 | 26.25 | -32.0 ±5.3 |
| | | 100 | 2.95 | 33.17 | 26.43 | -35.2 ±5.2 |
| | | 286 | 2.67 | 33.44 | 26.67 | -69.2 ±5.9 |
| OT5 | 17 Mar 2014 | 0 | 1.47 | 32.82 | 26.27 | -36.0 ±4.8 |
| | | 20 | 1.54 | 32.85 | 26.28 | -35.8 ±5.4 |
| | | 50 | 2.52 | 33.12 | 26.42 | -39.8 ±5.2 |
| | | 100 | 3.37 | 33.26 | 26.46 | -31.2 ±4.9 |
| | | 200 | 2.83 | 33.45 | 26.66 | -66.9 ±5.2 |
| | | 1026 | 3.04 | 34.34 | 27.35 | -199.2 ±2.9 |
| OT6 | 17 Mar 2014 | 0 | 2.43 | 32.72 | 26.12 | -44.3 ±3.4 |
| | | 20 | 1.59 | 32.74 | 26.19 | -44.9 ±3.2 |
| | | 50 | 1.90 | 32.94 | 26.33 | -45.8 ±3.0 |
| | | 100 | 2.77 | 33.14 | 26.42 | -58.2 ±2.9 |
| | | 200 | 2.37 | 33.41 | 26.67 | -73.7 ±3.3 |
| | | 1000 | 2.86 | 34.37 | 27.39 | -196.2 ±2.6 |
| ON7 | 16 Mar 2014 | 0 | 8.11 | 33.67 | 26.21 | -4.7 ±4.0 |
| | | 50 | 8.11 | 33.67 | 26.22 | 4.9 ±4.1 |
| | | 100 | 7.90 | 33.65 | 26.23 | -9.6 ±3.9 |
| | | 200 | 7.51 | 33.61 | 26.25 | 4.7 ±4.3 |
| | | 1000 | 2.94 | 34.41 | 27.42 | -192.3 ±3.8 |
| ON8 | 16 Mar 2014 | 0 | 8.15 | 33.67 | 26.21 | 8.2 ±5.0 |
| | | 20 | 8.15 | 33.67 | 26.21 | 1.4 ±2.9 |
| | | 50 | 8.14 | 33.67 | 26.21 | 5.9 ±4.3 |
| | | 100 | 7.94 | 33.66 | 26.23 | 0.8 ±3.2 |
| | | 200 | 6.95 | 33.54 | 26.27 | 0.3 ±3.0 |

Table 3.5. $\Delta^{14}C$ values in upper and lower pinnae, and their offset values at different sampling stations. Mean $\Delta^{14}C$ values for each station and pooled data were calculated using the mean values of each individual.

| Station | n | Individual code | Upper pinnae | | Lower pinnae | | $\Delta^{14}C$ offset (‰) |
|---|---|---|---|---|---|---|---|
| | | | $\Delta^{14}C$ (‰) | Error (1σ) | $\Delta^{14}C$ (‰) | Error (1σ) | |
| A2 | 2 | S1 | 17.6 | ±3.5 | -21.0 | ±4.1 | |
| | | | -1.7 | ±3.8 | -28.2 | ±3.0 | |
| | | | 11.4 | ±3.2 | -14.2 | ±2.6 | |
| | | S2 | -14.9 | ±3.0 | -38.4 | ±2.9 | |
| | | | -11.2 | ±3.2 | -32.1 | ±3.2 | |
| | | | 6.0 | ±4.4 | -18.7 | ±2.9 | |
| | | mean ± SD | 1.2 ± 11.2 | | -25.4 ± 6.1 | | 26.6 |
| A3 | 3 | S3 | 11.4 | ±4.2 | -19.3 | ±3.6 | |
| | | | -4.2 | ±3.0 | -10.8 | ±3.5 | |
| | | | -6.1 | ±2.9 | -25.8 | ±2.3 | |
| | | S4 | 6.6 | ±3.9 | -45.6 | ±4.5 | |
| | | | 3.0 | ±3.8 | -32.6 | ±3.9 | |
| | | | -5.7 | ±5.9 | -36.1 | ±4.0 | |
| | | S5 | 4.9 | ±3.4 | -22.5 | ±3.6 | |
| | | | 2.6 | ±5.4 | -16.9 | ±3.7 | |
| | | | -1.3 | ±3.8 | -14.4 | ±4.5 | |
| | | mean ± SD | 1.2 ± 0.9 | | -24.9 ± 11.5 | | 26.1 |
| A7 | 3 | S6 | -0.3 | ±3.7 | -32.6 | ±6.3 | |
| | | | 6.1 | ±3.5 | -35.3 | ±7.7 | |
| | | | 4.9 | ±3.5 | -3.3 | ±3.2 | |
| | | S7 | 9.2 | ±3.5 | -9.8 | ±3.1 | |
| | | | 17.5 | ±4.3 | -23.2 | ±3.3 | |
| | | | 5.5 | ±3.8 | -10.2 | ±3.2 | |
| | | S8 | 9.5 | ±3.7 | -18.5 | ±3.2 | |
| | | | 2.3 | ±4.2 | -29.8 | ±3.2 | |
| | | | -1.4 | ±4.0 | -28.0 | ±3.4 | |
| | | mean ± SD | 5.9 ± 4.2 | | -21.2 ± 1.4 | | 27.1 |
| pooled | 8 | mean ± SD | 3.0 ± 5.4 | | -23.6 ± 7.5 | | 26.6 |

Table 3.6. Spearman's rank correlation ($r_s$) between pinna positions and $\Delta^{14}C$ values.

| | Pinna position | | |
|---|---|---|---|
| | $\Delta^{14}C$ (‰) | | |
| Individual code | $r_s$ | *p* | n |
| S1 | -0.863 | < 0.001 | 13 |
| S3 | -0.660 | < 0.005 | 20 |
| S4 | -0.802 | < 0.005 | 13 |
| S6 | -0.579 | < 0.05 | 15 |
| pooled | -0.619 | < 0.001 | 61 |

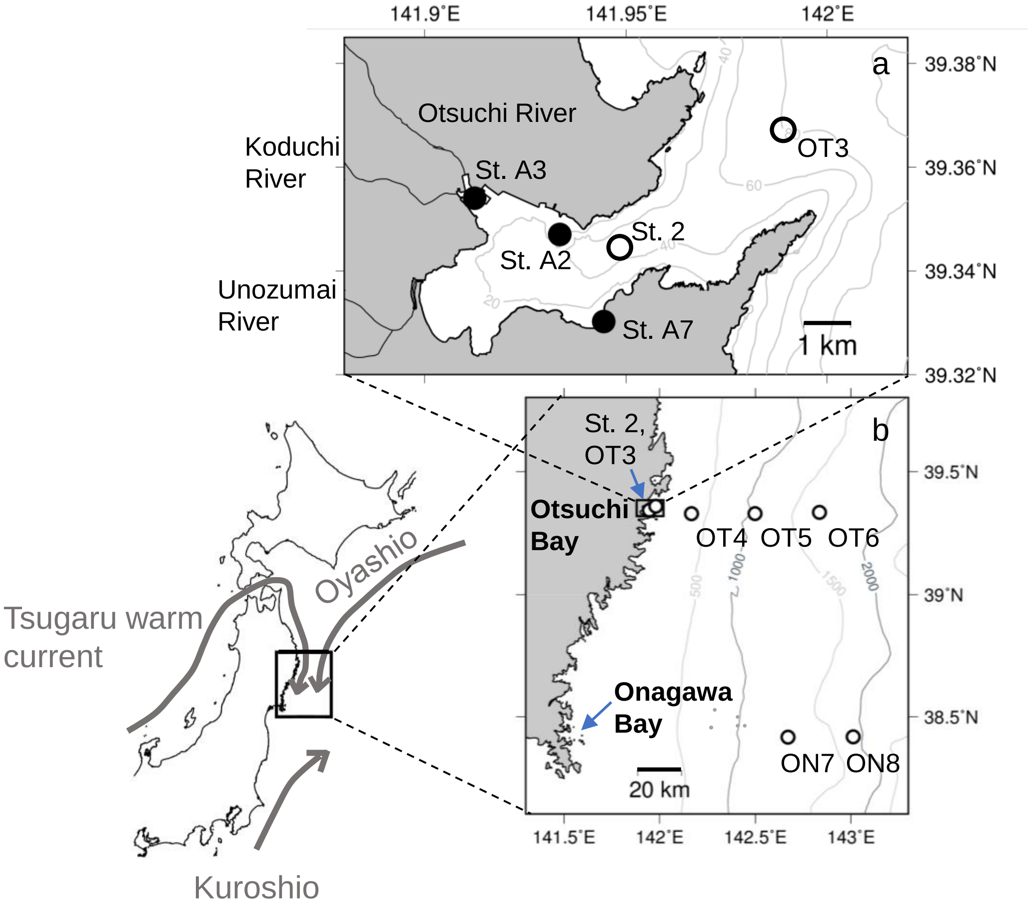

Fig. 3.1. a) *Undaria pinnatifida* cultivation sites (Sts. A2, A3, and A7) in Otsuchi Bay. b) Sampling stations for seawater DIC in the offshore region of the Sanriku coast.

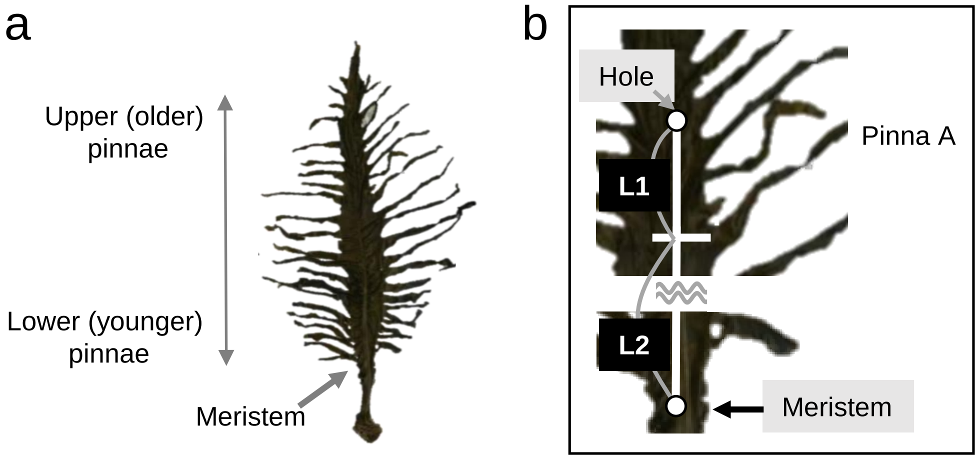

Fig. 3.2. a) *U. pinnatifida* sporophyte. New pinnae emerge near the meristem, and their position along the long axis of the blade reflects the chronological order of their formation. b) The position of pinna A ($L_a$) was defined as the distance (cm) from the punch hole to the base of pinna A after normalization (see chapter 3 Materials and Methods).

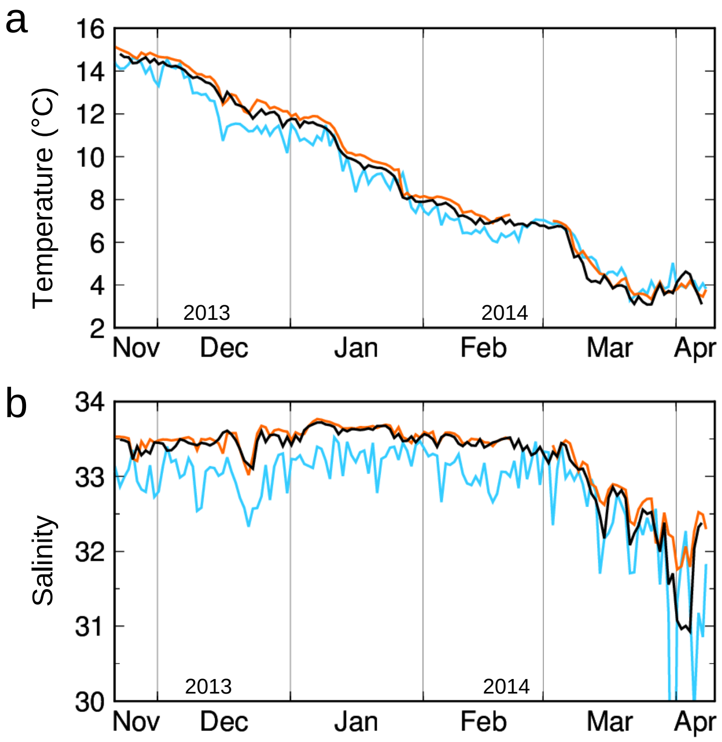

Fig. 3.3. Time series of daily average (a) temperature and (b) salinity at the cultivation sites (depth: 3 m) from November 21 to April 8. Data collected at Sts. A2, A3, and A7 are indicated by black, orange, and blue lines, respectively.

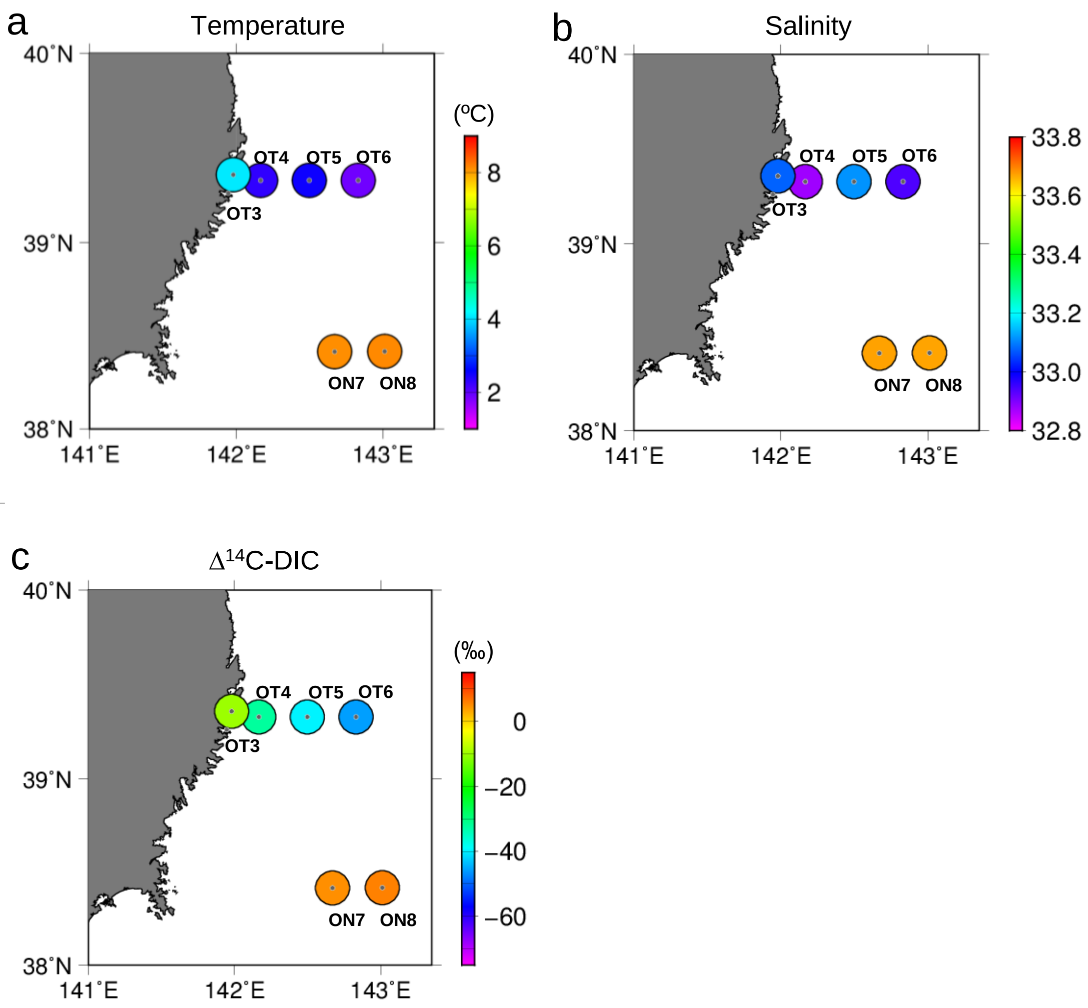

Fig. 3.4. Spatial distribution of (a) temperature, (b) salinity, and (c) $\Delta^{14}$C-DIC collected off the Sanriku coast on March 16–17. Data shown were collected at depths of 50 and 60 m.

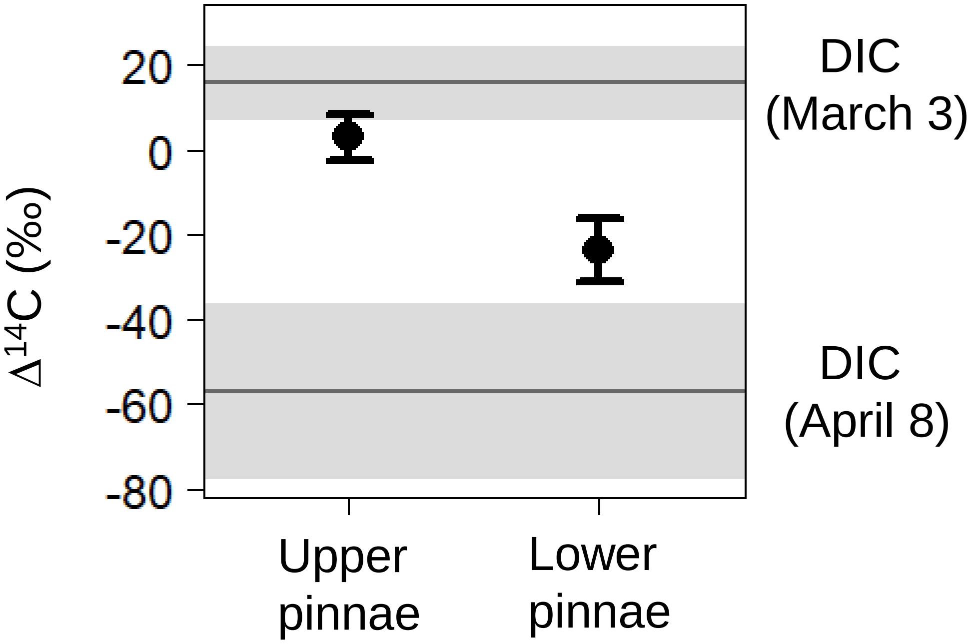

Fig. 3.5. $\Delta^{14}C$ values for upper (near the punch hole) and lower (near the meristematic region) *U. pinnatifida* pinnae. Solid circles with error bars indicate means and standard deviations of $\Delta^{14}C$ for upper and lower pinnae (n = 8). Gray lines and shaded regions represent means and standard deviations of $\Delta^{14}C$-DIC values, respectively, for March 3 (when holes were punched) and April 8 (when individuals were harvested).

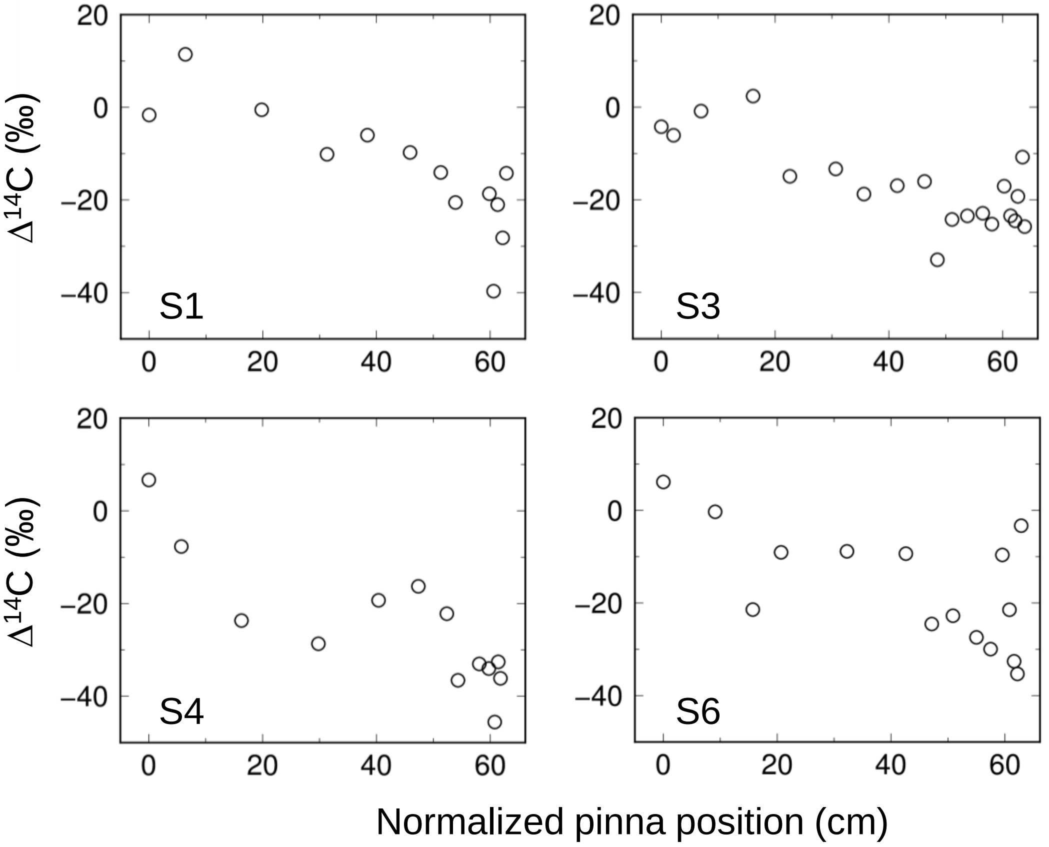

Fig. 3.6. Relationship between normalized pinna position and Δ$^{14}$C for four individuals. Dashed lines are trend lines derived from linear regression (see Table 3.6 for statistical results of the rank correlation between pinna position and Δ$^{14}$C).

## Chapter 4

# Contributions of the Oyashio and Kuroshio system to the provision of organic carbon for deep-sea benthic megafauna in the Sanriku region, the western North Pacific

本章については、5年以内に雑誌等で刊行予定のため、非公開。

## Chapter 5

# The ages of organic carbon in benthic invertebrates, sediments and particulate organic matter in Otsuchi Bay

本章については、5年以内に雑誌等で刊行予定のため、非公開。

# Chapter 6

# General discussion

## 6.1 Summary of the findings of this study

In this study, I investigated $\Delta^{14}C$ values of DIC, POM, SOM, macroalgae, and benthic invertebrates in the Sanriku region in order to test the following four hypotheses relevant to the carbon cycles in the Sanriku region. (1) the Oyashio and Kuroshio are major carbon sources in the Sanriku region and can be distinguished by $\Delta^{14}C$; (2) Oyashio-derived carbon can be detected using $\Delta^{14}C$ values of benthic primary producers (macroalgae); (3) Oyashio-derived carbon is a significant carbon source for offshore megabenthos because of its high productivity; (4) aged organic matter is incorporated into benthic consumers at a higher trophic level in the coastal ecosystem. In this section, I summarize the results of each chapter based on these hypotheses.

### Chapter 2: The Oyashio system and Kuroshio system were the major carbon sources in the Sanriku region and could be distinguished by $\Delta^{14}C$ (hypothesis 1 was supported)

In this chapter, I described the spatio-temporal variability of $\Delta^{14}C$-DIC value off the Sanriku region and found that the value was primarily influenced by the mixing of Oyashio and Kuroshio water masses. It should be emphasized that the data that I collected represent the first results demonstrating that the Sanriku coastal region has two major carbon sources which can be distinguished by $\Delta^{14}C$ signatures: warm waters (Kuroshio, Tsugaru, and surface layer waters) with high $\Delta^{14}C$ values (ca. 31‰), and cold waters (Oyashio and cold Oyashio) with low $\Delta^{14}C$ values (ca. –66‰). These data provide a strong basis for the evaluation of the role of the Oyashio system and Kuroshio system in supporting primary producers (chapter 3) and benthic megafouna (chapter 4) in the Snariku coastal region.

### Chapter 3: Oyashio-derived carbon could be detected using $\Delta^{14}C$ values of benthic primary producers (macroalgae) (hypothesis 2 was supported)

Cultivation of macroalga (*Undaria pinnatifida*) was conducted in Otsuchi Bay on the Sanriku coast. The $\Delta^{14}C$ values of pinnae at different positions were compared with their $\Delta^{14}C$-DIC values during photosynthesis. During the cultivation period, Oyashio intrusion occurred from early March to early April, accompanied by a reduction in bay water $\Delta^{14}C$-DIC. The $\Delta^{14}C$ of the pinnae reflected $\Delta^{14}C$-DIC, as pinnae formed in early March had significantly higher $\Delta^{14}C$, compared to pinnae formed in early April. These results indicated that the $^{14}C$-depleted signal of the Oyashio is recorded in the $\Delta^{14}C$ of *U. pinnatifida* pinnae. Importantly, these results demonstrate the utility of $\Delta^{14}C$ for examining the dependency of consumers on food containing carbon from different water masses, as macroalgal $\Delta^{14}C$ signatures should be transferred to their consumers.

### Chapter 4: Oyashio-derived carbon was a significant carbon source for offshore megabenthos presumably because of its high productivity, although the extent of the dependency on Oyashio differed among different taxa (hypothesis 3 was supported)

In this chapter, I evaluated the relative contribution of the Oyashio system and Kuroshio system to the food provisioning for benthic megafauna in the deep seafloor using $\Delta^{14}C$. The most important findings include that the estimated contribution of Oyashio-derived carbon to such diets was high (generally exceeded 50%) despite the fact that Oyashio generally intrudes into the surface layer in the studied area for only a short period (1–2 months of the year). This high contribution of Oyashio is probably explained by its high productivity. My data also revealed that the importance of Oyashio-derived carbon differed among taxa, which suggested that the food niche differed among taxa. These findings demonstrate that the radiocarbon approach can reveal novel aspects in the carbon cycle through the benthic-pelagic couplings in the Sanriku area.

**Chapter 5: Radiocarbon signals indicated the widespread occurrence of aged carbon in POM and SOM of Otsuchi Bay. However, the data did not support the hypothesis that aged organic matter is incorporated into benthic consumers at a higher trophic level in Otsuchi Bay. (hypothesis 4 was not supported)**

In this chapter, I investigated the age of the organic carbon that supports benthic invertebrate biomass in Otsuchi Bay using $\Delta^{14}C$. The $\Delta^{14}C$ values of invertebrates were generally similar to those of DIC. The $\Delta^{14}C$ values of SOM and POM varied much more widely among locations and seasons than among DIC and benthic invertebrates. These data indicated that benthic invertebrates in this bay assimilate only modern carbon originating from contemporaneous autotrophs, despite the widespread occurrence of old carbon in the SOM and POM. Thus, my results did not support the hypothesis that the aged carbon enters into the benthic ecosystem in Otsuchi Bay.

### 6.2 Future perspectives: the use of radiocarbon for evaluating changing carbon cycles in Sanriku coastal ecosystems

My data revealed that radiocarbon is a powerful tracer to evaluate the role of Oyashio intrusion in supporting Sanriku coastal ecosystems. In fact, the data presented in chapter 3 is the first to examine the timing of Oyashio intrusion using the position-dependent variability in $\Delta^{14}C$ signatures in macroalgae (chapter 3). Furthermore, the results of chapter 4 provided new insights into the dependency of deep-sea benthic megafauna on Oyashio cold waters and Kuroshio warm waters.

These findings have important implications for the future research concerning possible ecological changes in the Sanriku region in response to the changes in oceanographic conditions associated with global climate change. In recent years, the southernmost latitude of Oyashio intrusion remarkably shifts northward (e.g., Tatebe and Yasuda 2005). This oceanographic change concurrently with global warming may cause a reduction of nutrient supply and an increase in surface water temperature in the Sanriku region and eventually may affect the deep-sea benthic community through the benthic-pelagic coupling. Because the dependency on the Oyashio derived carbon differed among taxa and locations, it can be expected that the species composition and growth rate of benthic communities would drastically be affected by the mixing property on the surface. To better understand the role of oceanographic conditions in sustaining deep-sea benthic ecosystem productivity, more intensive surveys including long-term monitoring, spatiotemporal analysis, and accumulating basic knowledge about benthic animals are required. The radiocarbon approach that I developed in this research may provide a powerful tool for fulfilling such research needs. Because $\Delta^{14}C$ values are straightforward indicator of the contribution of Oyashio-derived carbon to the biomass production, as demonstrated in this study, a systematic, time-series monitoring of $\Delta^{14}C$ values of benthic organisms over years may help investigate the change in the influence of Oyashio on the regional productivity. If the influence of Oyashio will decrease with the progress of on-going changes in oceanographic conditions (e.g. the intensification of Kuroshio in this region), I would expect a systematic increase in $\Delta^{14}C$ values of organisms in this region. I suggest that the combination of $\Delta^{14}C$ approach with other biological (e.g., body size, abundance, growth rate) and biochemical indicators (e.g., metabolic enzymes, RNA/DNA; Dahlhoff 2004) is especially useful and will allow us to evaluate how the changes in Oyashio influence lead to the changes in growth and physiological conditions of organisms.

The radiocarbon approach should be also useful for the future research concerning the role of aged carbon in coastal ecosystems. Although my data presented in chapter 5 failed to detect significant signals of aged carbon in benthic invertebrates in Otsuchi Bay, we should not simply generalize these results for other environments/organisms or even for benthic invertebrates in Otsuchi Bay. Recent studies have reported conflicting results regarding the role of aged carbon in aquatic food webs (Guillemette et al. 2017). To date, the general consensus relevant to this matter is that coastal systems receive terrestrial inputs of organic carbon of various sources and ages (e.g., Blair and Aller 2012). Does this aged carbon enter into food webs? How important is this input for food webs? Is the aged carbon directly assimilated by invertebrates, or is it first assimilated by microbes and then transferred to higher trophic level organisms via microbial food chain? As such, this issue covers a broad range of topics in aquatic ecology and biogeochemistry. I argue below that future studies should explore this issue in greater details with an aid of radiocarbon approach.

There has been a growing concern that climate change would alter the carbon cycle in global ecosystems (Scavia et al. 2002; Schuur et al. 2008; Hoegh-Guldberg and Bruno 2010; Bauer et al. 2013). The climate change and anthropogenic impacts may lead to the mobilization and export of aged terrestrial carbon, especially in high latitude regions where permafrost, glaciers and ice-sheets are rapidly melting to discharge more aged carbon to aquatic systems (Schuur and Abbott 2011; Hood et al. 2015). Recent studies have increasingly suggested that some of these aged materials are readily metabolized by microbes and incorporated into the secondary production (Bardgett et al. 2007; Hågvar and Ohlson 2013; Fellman et al. 2015). Climate change may also alter the frequency and intensity of hurricane and tropical storms, as well as patterns of rainfall and subsequent delivery of freshwater and nutrients to coastal environments (Scavia et al. 2002; Park et al. 2010; Intergovernmental Panel on Climate Change 2014). Furthermore, anthropogenic impacts such as deforestation, agricultural intensification and the injection of human wastewater are known to increase the age of organic matter in rivers (Butman et al. 2015), which in turn may result in increasing inputs of old carbon from land to the ocean (Ver et al. 1999; Regnier et al. 2013). These environmental changes are predicted to have impacts on the structure and function of aquatic ecosystems (Scavia et al. 2002).

The above information strongly suggests that it is likely that climate change is altering the quantity and quality of terrestrial materials transported from land to coastal environments. I argue that the evaluation of the impacts of such changes to coastal food webs is an important issue. As demonstrated in this study, the radiocarbon technique, with the combination of stable isotopes, must provide a powerful tool to clarify the dynamics of organic matter with different ages (fresh vs. old) and origins (marine vs. terrestrial). In the future, a long-term study using the $^{14}C$ approach is expected to play an important role in gaining knowledge about the alteration of carbon cycles and biotic communities at the interface of the land and sea.

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