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Dissolved methane distribution in seawater and its controlling factors in the polar regions

（極域における海水中メタンの分布とその制限因子に関する研究）

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2018
Acknowledgment

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Sapporo, 18th August 2018

Bùi Thị Ngọc Oanh
ABSTRACT

Methane (CH$_4$) is a potent greenhouse gas and plays significant roles in both tropospheric and stratospheric chemistry. During the last two centuries, mixing ratio of atmospheric CH$_4$ has increased by 1000 ppb and reached to 1834 ppb in 2015 as a result of anthropogenic activities. It is known that ocean acts as one of the sources of atmospheric methane and the methane flux depend on the oceanic region owing to the difference in biological activities and physical condition. For example, the region characterized by high productivity releases more CH$_4$ to the atmosphere than the other regions because CH$_4$ is produced via microbial methanogenesis in anaerobic environments from bacteria in organic particles or the gut of zooplankton. Until now, some works have implemented to measure CH$_4$ concentration in the polar regions where the impact of climate change is believed to be strongest in the world ocean. However, the data scarcity causes the uncertainty of the CH$_4$ distribution in the polar oceans, its controlling factors and the contribution of the polar oceans to global CH$_4$ sea-air fluxes. I, therefore, used the high-resolution dataset to detect oceanic CH$_4$ in seawater to reduce the uncertainty from the previous estimations.

The Southern Ocean is one of the most biologically productive regions among the world’s oceans, where is characterized by high biomass of zooplankton, Antarctic krill, and salps, from which large amount of CH$_4$ production could be expected. A cavity ring-down spectroscopy (CRDS) system coupled with a shower-head type equilibrator was used to obtain quasi-continuous underway measurements of the mixing ratio of oceanic CH$_4$ in seawater during legs 2 and 3 of cruise MR12-05 of R/V Mirai in the Southern Ocean from late November 2012 to mid-February 2013. High CH$_4$ saturation ratio (SR, %) occurred in the lower latitudes including coastal area north of sub-antarctic front (SAF). SR decreased gradually and monotonously between SAF and southern limit of upper circumpolar deep water (SBDY), and occasionally decreased lower than 100% due to vertical mixing/upwelling in high latitudes south of polar front (PF). A good correlation between SR and apparent oxygen utilization (AOU) was found south of PF, $SR = -0.294 \times AOU + 100.093$ ($n = 1549, r^2 = 0.89$). On the basis of SR-AOU relationship, I have calculated the sea-air CH$_4$ flux during December to February in the entire of the Southern Ocean (south of 50°S). The sea-air CH$_4$ emission was estimated to be 0.027 Tg-CH$_4$ yr$^{-1}$ in December, 0.04 Tg-CH$_4$ yr$^{-1}$ in January, and 0.019 Tg-CH$_4$ yr$^{-1}$ in February. From my estimation, south of 50°S, the average flux of CH$_4$ in austral summer is 0.024 Tg-CH$_4$ yr$^{-1}$, which is account for a minor contribution (less than 1% of the global oceanic release of 4-15 Tg yr$^{-1}$) of CH$_4$ to the atmosphere.
The Arctic Ocean is particularly the most sensitive to global warming, for example, Arctic sea ice thickness and extent are declining, due to increasing sea-surface temperature. In the Arctic Ocean, a massive CH\(_4\) hydrates from marine sediments release and/or methanogenic CH\(_4\) producing in anaerobic environment with the presence of high organic matter on the seafloor and then diffusion into water column was examined. However, the vertical profile of CH\(_4\) distribution is still scarce, so it is needed to be examined for comprehension of CH\(_4\) dynamics in the water column. I examined vertical profiles of CH\(_4\) distribution inside and outside of a warm-core eddy during Leg. 1 of the cruise MR15-03 of R/V Mirai in the Arctic Ocean in late summer/early fall 2015. Because a coherent mesoscale eddy is one of the possible mechanisms for transporting the shelf water from Chukchi Sea into the Canada Basin interior, I hypothesized that the warm-core eddy transported nutrients as well as dissolved CH\(_4\) and impacted the distribution of CH\(_4\). In this study, the existence of the warm-core eddy that it would carry nutrients as well as dissolved CH\(_4\) and impact on CH\(_4\) distribution. Thus, seawater samples were collected to obtain detailed vertical profiles of CH\(_4\) distribution in the southwestern Canada Basin. High CH\(_4\) concentrations were found at the bottom on the shelf, where located outside the warm-core eddy. Saturation of CH\(_4\) in that water was high 947% respecting to atmospheric CH\(_4\). I also found that sub-surface CH\(_4\) peaks within the radius of maximum velocity of the eddy were broader spread in-depth than those outside of the eddy. The presence of the eddy was likely the controlling factor responsible for subsurface CH\(_4\) peaks inside the warm-core eddy. This study indicates that eddies play a crucial role in controlling CH\(_4\) distributions and transport it from shelf water to the southwestern Canada basin.

In addition, extent of sea ice in the Arctic has been decreasing while sea ice acts as physical barrier. Removal of this barrier directly affects sea-air exchange of CH\(_4\). I investigated CH\(_4\) distribution in the Arctic Ocean under two conditions: in the shelf water and sea ice cover region in order to evaluate the influence of sea ice coverage on CH\(_4\) emission. During the cruise of IBRV ARAON (ARAON-07B) in August 2016, seawater samples were collected from the surface to the bottom to detect the vertical profiles of CH\(_4\) distribution in the Bering, Chukchi Seas and the Arctic Ocean. Over the whole region, dissolved CH\(_4\) concentration ranged from 3.5-23.1 nmol kg\(^{-1}\) in the surface water, which was supersaturated (range: 124.7-604.6%) to the atmospheric CH\(_4\). Observed CH\(_4\) concentration increased with depth at the shallow water. High dissolved CH\(_4\) concentration was found at the Chukchi shelf slope resulted from high \textit{in situ} methanogenesis of organic matter. In the sea ice cover region, CH\(_4\) concentration increased at the subsurface water (50-100 m) and decreased with depth to
the bottom. Low CH$_4$ was observed at the deeper water (> 200 m) in sea ice cover region. Dissolved CH$_4$ varied in the distinct water masses (PSW, PWW, ACW, MW and AW). Relations between CH$_4$ and nutrients as well as its precursors are compared under the two conditions. High CH$_4$ concentrations observed at surface seawater were consistent with high sea ice concentrations. This investigation allows us to gain some insights into the role of the sea ice on CH$_4$ concentration and the flux.
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LIST OF ABBREVIATIONS

CH₄  Methane
N₂O  Nitrous Oxide
DMS  Dimethylsulphide
DMSP Dimethylsulfoniopropionate
Pdw  Pacific-derived water
Adw  Atlantic-derived water
ACW  Alaskan Coastal Water
PSW  Pacific Summer Water
PWW  Pacific Winter Water
AW   Atlantic Water
MW   Meltwater and River water
CRDS Cavity Ring-Down Spectroscopy
GC   Gas Chromatography
SR   Saturation
CHAPTER 1:
GENERAL INTRODUCTION

1.1 Generally introduction CH₄ in the ocean

1.1.1 Introduction to CH₄

After carbon dioxide (CO₂), methane (CH₄) is an effective greenhouse gas and plays an important role in the Earth radiative and chemical balance, contributing 15-20% of atmospheric radiative forcing (IPCC, 2013). CH₄ is the most abundant reactive trace gas in the troposphere, and its reactivity is important to both of tropospheric and stratospheric chemistry (Cicerone and Oremland, 1988). Thus, CH₄ is one of the factors in consideration of global climate change (IPCC, 2001). Average concentration of atmospheric CH₄ is determined mainly by the balance between emission from the surface and destruction by hydroxyl free radicals (OH) in the troposphere (Wuebbles and Hayhoe, 2002). There is a recent evidence that there has been a dramatic increase in the tropospheric CH₄ mixing ratio over 100-year timescale. During the last two centuries, this ratio has increased by 1000 ppb, reached up to approximately 1850 ppb as a result of anthropogenic activities (https://www.esrl.noaa.gov/gmd/ccgg/trends_ch4/; Dlugokencky et al., 1994). CH₄ is increasing at a variable rate that is not clearly understood which is reflected on changing of sources and sinks strength (Dlugokencky et al., 1994). Although the contribution of greenhouse gases to radiative forcing is clear, the cycle of this gas in various reservoirs is still poorly understood. Hence, understanding of the global CH₄ budget and CH₄ cycling is a primary research objective in the Earth Science.

1.1.2 CH₄ sources and sinks

The sources can be organized into two main categories such as natural and anthropogenic sources. Natural sources consist of oceans, fresh water, gas hydrates, termites, natural forest fires, boreal and tropical wetlands including rice paddies. Another one is from anthropogenic activities including from fossil fuels, energy use, landfill, waste treatment, and ruminant animals, and biomass burning (Wuebbles and Hayhoe, 2002).

The ocean has only a minor role in the global CH₄ budget; oceanic emissions account for a few percentages of all natural and anthropogenic sources (Cicerone and Oremland, 1988; Conrad and Seiler, 1988; Crutzen and Zimmermann, 1991; Bange et al., 1994). On the other hand, a small region of the ocean is a sink of CH₄. Although major sources and sinks of
atmospheric CH$_4$ have been identified, significant uncertainties remain in estimations of the total earth and atmospheric budgets of CH$_4$ (Saunois et al., 2016).

CH$_4$ is produced through anaerobic methanogenesis of organic matters in sedimentary layer. Released CH$_4$ from sediments diffuses into seawater by bubbling and then oxidizes in the water column. Within the aerobic water column, CH$_4$ is produced by microbial methanogenesis in anaerobic environments and by bacteria in organic particles (Karl and Tilbrook, 1994), or within digestive tracts of organisms (de Angelis and Lee, 1994). CH$_4$ distribution is often controlled by biological production and oxidation. Oxidation processes and sea-air exchanges act to maintain CH$_4$ concentration near atmospheric equilibrium (Hanson and Hanson, 1996; Reeburgh, 2007; Grundward et al., 2009). Oxidation process in aerobic environments converts CH$_4$ into CO$_2$ and water (see Fig. 1.1). Fig. 1.1 represents microbial processes of organic matters (OM) transformation in marine anoxic sediments and emission to an anaerobic/aerobic CH$_4$ oxidation in the water column. Other sources of CH$_4$ may come from freshwater runoff from regions with anaerobic sediments containing hydrocarbon seeps or destabilized gas hydrates (Naqvi et al., 2010). Recently, CH$_4$ is produced by the cleavage of methylated substrates by bacteria or phytoplankton (Karl et al., 2008; Damm et al., 2010). Dissolved CH$_4$ concentration in the ocean depends on the magnitude of aerobic/anaerobic microbial production and oxidation so that the ocean can be a net source or sink. Estimation of strength of both production and consumption of CH$_4$ are difficult to make precisely quantification because of predictions of changing the environmental conditions such as sea ice cover, ocean biogeochemistry and so on, so it is essential for evaluating of contribution of oceanic CH$_4$ fluctuation to the atmosphere.

On the contrary, there are one major and two minor sinks for tropospheric CH$_4$, which CH$_4$ is removed from the atmosphere through chemical reaction. Reaction with the hydroxyl radical (OH) is a main process of removal of almost 90% of the total sink (~90%) (R1) (IPCC, 1996; Wuebbles and Hayhoe, 2002). A lifetime of CH$_4$ in the atmosphere is determined by the rate of this loss process, which is about 12 years. It is much shorter than a lifetime of carbon dioxide (5-200 years) (IPCC, 2013; https://www.ipcc.ch/ipccreports/tar/wgl/016.htm). Oxidation of CH$_4$ in the atmosphere (in the troposphere and the lower stratosphere) through reactions with NO$_x$ compounds lead to enhance ozone (O$_3$) formation as well as greenhouse gases from CH$_4$ emission (Isaksen et al., 2011) with the existence of N$_2$ molecule (M) and solar photon flux ($h\theta$) as follow.

$$(R1) \text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O} \quad (R2) \text{CH}_3 + \text{O}_2 + M \rightarrow \text{CH}_3\text{O}_2 + M$$
(R3) \(CH_3O_2 + NO \rightarrow CH_3O + NO_2\)  
(R4) \(CH_3O + O_2 \rightarrow CH_2O + HO_2\)  
(R5) \(CH_2O + h\theta \rightarrow CO + H_2\)  
(R6) \(CH_2O + h\theta \rightarrow CHO + H\)  
(R7) \(CH_2O + OH \rightarrow H_2O + CHO\)  
(R8) \(CHO + O_2 \rightarrow CO + HO_2\)  
(R9) \(CO + OH \rightarrow CO_2 + H\)  
(R10) \(H + O_2 + M \rightarrow HO_2 + M\)  
(R11) \(NO + HO_2 \rightarrow NO_2 + OH\)  
(R12) \(NO_2 + h\theta \rightarrow NO + O\)  
(R13) \(O + O_2 + M \rightarrow O_3 + M\)

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**Fig. 1.1** The sketch is representing microbial processes of organic matter transformation in marine sediments. Organic matters (OM) is represented by \(CH_2O\), deposited on the seafloor is aerobically degraded to \(CO_2\) and \(H_2O\). In the sulfate zone, OM is anaerobically transformed by fermentation to hydrogen (\(H_2\)), carbon dioxide (\(CO_2\)) and smaller organic compounds as acetate (\(CH_3COOH\)). \(CH_4\) may be anaerobically and aerobically oxidized or emitted to the water column.

### 1.2 Polar regions under climate change

Polar regions include the Arctic Ocean and the southern on the continent of Antarctica, are well-known covered by sea ice and ice, respectively. This area is very low temperature in winter, even in summer, many areas remain below freezing. Most of the surface water remains frozen state year-round (IPCC, 2007). Two polar regions have experienced remarkably different climate changes in recent decades. The IPCC report indicated that some of the largest...
changes which are expected to happen at high latitudes over the next century. Notably, over recent decades changing in sea ice extent has been observed different in the two polar regions. A marked reduction in sea-ice extent in the Arctic has reached minima in late summer, the extent of Antarctic sea ice has increased by a small amount (Turner and Overland, 2009) or remains steady (Maksym et al., 2012). In Western Antarctica, rates of warming are higher (Vaughan et al., 2003) with decreasing sea-ice (Stammerjohn et al., 2008) and retreating ice shelves (Wouters et al., 2015) than Eastern Antarctica. Further, a seasonal ice-free ocean could influence on Arctic ecology and climate, enhancement of solar irradiance, increase mixing, and reduce the albedo of the Arctic Ocean during boreal summer (IPCC, 2013).

Global average temperature increases up to 1-2°C over a few decades (Thorpe et al., 1996, https://www.epa.gov/climate-indicators/climate-change-indicators-us-and-global-temperature). Bracegirdle et al. (2008) found that temperatures across the Antarctic were expected to increase by about 0.33±0.1°C per decade on land and 0.26±0.1°C per decade in the ocean/sea-ice zone. Around East Antarctica sea ice is lost, the warming is predicted to be about 0.5°C per decade. Increase in annual mean temperature across the Arctic is expected with a value of 0.6-0.8°C per decade over the northern parts of the continents and with a value of 1°C per decade over the Arctic Ocean (Solomon et al. 2007).

Those changes affect the global warming following in biology, chemistry, and ocean circulation of the ocean, so these changing may influence on the carbon cycles or biogeochemical cycles. Examination of Arctic and Antarctic CH₄ is vital to rapid climate changes. Besides, observed CH₄ concentration also increases in recent as shown in the previous studies. Increasing CH₄ emission helps to trigger climate change or how it responds to rising atmospheric temperature and sea surface temperature.

1.3 Dissolved methane distribution in seawater in the polar regions

Dissolved CH₄ in surface ocean water tends to be supersaturated with respecting to atmospheric CH₄(Conrad and Seiler, 1988; Crutzen and Zimmermann, 1991; Bates et al., 1993; Tilbrook and Karl, 1995). Dissolved CH₄ concentrations are supersaturated throughout the equatorial and tropical regions of the Pacific Ocean (Bates et al., 1996; Yoshida et al., 2011), but both supersaturation and undersaturation are known in the extratropics (Kelly and Jeffrey, 2002) and at high latitudes (Bates et al., 1996; Yoshida et al., 2011). In the pelagic zone, CH₄ is supplied via biological production and removed from ocean water by microbial oxidation and by sea–air flux (Grunwald et al., 2009). In productive coastal areas, large amounts of CH₄,
which account in part for the high contribution of coastal areas and estuaries to the sea–air flux of CH$_4$ (Bange et al., 1994), are produced by methanogenesis in buried sediment layers. An enhancement of CH$_4$ fluxes in coastal upwelling regions likely contribute to the atmosphere on global scale (Rehder et al., 1999). CH$_4$ fluxes from the coastal areas occupy about 1/10 of the open ocean area, the degree of supersaturation is about 1 order of magnitude higher than that in the open ocean (Bange et al., 1994).

The Arctic area is well-known to be regarded as a great storage of CH$_4$ (IPCC, 2007; IPCC, 2013; McGuire et al., 2010). Large amount of CH$_4$ sources exists (e.g., sediment release, CH$_4$ hydrates, subsea permafrost), and they directly contribute to the water column as well as the atmosphere. Arctic continental shelves are sites of meaningful CH$_4$ production and emission, super-saturation CH$_4$ up to 125% was documented in the surface water in the Chukchi Sea (Savvichev et al., 2007; Hirota et al., 2009). High levels of CH$_4$ in the atmosphere of the Laptev Sea and the East Siberian Sea with an average concentration were 2.97 ppm and 2.66 ppm, respectively (Shakhova et al., 2010), suggesting that unusually sizeable CH$_4$ source from here. The Laptev Sea and the East Siberian Sea are wide and shallow (averaging 50 m) (Jakobsson, 2002) and CH$_4$ is underlain by thawing permafrost (Nicolsky et al., 2012). Released CH$_4$ could originate from either deep thermogenic sources (Cramer and Franke, 2005) or released and transported from thawing permafrost on land (Charkin et al., 2011). The elevated CH$_4$ concentration of microbial CH$_4$ in sediment with enhanced bottom water CH$_4$ concentration were observed in the Beaufort Sea. Flux of CH$_4$ from the entire deep Arctic Ocean (~ 8.1×10$^6$ km$^2$) resulted from 0.36 Tg CH$_4$ yr$^{-1}$ (Lorenson et al., 2016). High CH$_4$ flux of 18-48 Tg yr$^{-1}$ in shallow water from seabed is estimated (Hornafius et al., 1999) contributing CH$_4$ distribution in the water column. While an average annual CH$_4$ input into the atmosphere of Cicerone and Oremland. (1988) was about 560 Tg, their emission rates were lower than the number of that at eastern Siberian Arctic shelf of 3.7 mg CH$_4$ m$^{-2}$ d$^{-1}$ attributed to subsea permafrost degradation reported by Shakhkova et al. (2010).

The Southern Ocean is the most biologically productive region with high biomass of zooplankton, Antarctic krill and salps (Knox, 2007) suggesting large amount of CH$_4$ in the Southern Ocean. High CH$_4$ concentration at high latitudes is suggested by enhancement of biological CH$_4$ production (Heeschen et al., 2004). Also, higher CH$_4$ concentration concurrently existed with an abundance of chlorophyll-$a$ concentration (Yoshida et al., 2011). In the surface water of the Southern Ocean, oceanic CH$_4$ has been reported to be supersaturated and undersaturated with respecting to atmospheric CH$_4$ (Tilbrook and Karl, 1994; Bates et al.,
1996; Heeschen et al., 2004; Yoshida et al., 2011). The Southern Ocean has contributed minor sources and sinks to the atmosphere comparing to the Arctic Ocean. Air-sea exchange is a primary source of CH$_4$ in the West Southern Ocean and mixing between surface water and warm water from deep water upwell controls distribution of CH$_4$ in the surface water (Heeschen et al., 2004).

### 1.4 Relation of CH$_4$ versus precursors

Significant CH$_4$ production coincides with existence of high organic materials in sedimentary layer in the anaerobic environment (Reeburgh, 2007) while in oxygenated water methanogens produce CH$_4$ within suspended particulate matters or within the anoxic center of sinking particles (Sasakawa et al., 2008; Forster et al., 2009) which accumulate in the pycnocline (Karl and Tilbrook, 1994). Correlation between CH$_4$ and chlorophyll-$a$ concentration (Damm et al., 2015a; Yoshida et al., 2011) has been found.

In the Arctic, distinct post-bloom nutrient limitation in Atlantic- and Pacific-dominated sectors are examined. Limitation of nutrient as a possible regulator of CH$_4$ in production in surface water has been investigated recently (Damm et al., 2010) while CH$_4$ excess in the ocean surface relative to the atmospheric equilibrium (Damm et al., 2015b). Different nutrient limitation can stimulate the growth of bacterioplankton assemblages and sequential organic matter, biogeochemical cycling of carbon (Thingstad et al., 2008). CH$_4$ is converted from methyl-phosphonate (MPn) with a phosphate-stress condition in subtropical gyres (Karl et al., 2008) but converted from dimethylsulfoniopropionate (DMSP) in polar oligotrophic water with nitrate-stress environment (Damm et al., 2010). Methanogens that produce CH$_4$ by catabolism of methylated compounds are microorganism mainly consisting of Archaea. Methylotrophic bacteria use methylated compounds including methylated sulfur compounds such as DMSP and dimethyl sulfide (DMS) (Neufeld et al., 2008; Florez-Leiva et al., 2013). Both DMSP and DMS are S- and C-containing organic compounds that are biosynthesized by phytoplankton, and assimilated and degraded by bacterioplankton (Kiene et al., 2000). DMSP transforms to DMS which influences global temperature with cooling effect (Andreae, 1990). The DMSP degradation supply precursors for the CH$_4$ formation suggesting methylotrophic methanogenesis as the principal pathway (Tallant and Krycki, 1997; Damm et al., 2010).
1.5 Physical and biogeochemical factors impact CH₄ distribution

The main factors controlling CH₄ supersaturation in tropical and extratropical regions are equatorial upwelling and seasonal variations of sea surface temperature (SST), respectively (Bates et al., 1996). SST affects CH₄ production rate and CH₄ oxidation rate (Hanson and Hanson, 1996). Maximum CH₄ growth rate is active in seawater temperature of 15°C. In the polar regions, seawater is cool; it may limit CH₄ production rate and oxidation rate compared to the warm seawater.

Water masses in the Southern Ocean are characterized by physical processes and biogeochemical processes (Orsi et al., 1995). In the Southern Ocean, maximum CH₄ concentration exists in a subsurface layer between 10°S and Sub-Tropical Front (STF, 47°S). In the south of STF, the maximum CH₄ concentration tends to be high by biogenic CH₄ production (Yoshida et al., 2011). A good correlation of CH₄ concentration and water density between 10°S and PF (Polar Front) in the Southern Ocean and in the eastern Arctic Ocean suggest a significant role of difference in density between particles having anaerobic microenvironment and seawater (Yoshida et al., 2011; Fenwick et al., 2017). CH₄ is produced by the abundance of Antarctic krill (Nicol et al., 2000) reported in the cool surface water in the south of Antarctic Circumpolar Current. Correlation between chlorophyll-a concentration and CH₄ concentration is found (Yoshida et al., 2011).

In the Arctic Ocean, high CH₄ concentration in colder and denser water from Pacific Winter Water has been found in the Chukchi shelf-water (Fenwick et al., 2017). Elevated CH₄ concentration is produced in anoxic sediment and released into the water column as bubble from sediment (Leifer and Patro, 2002). Then it is transported from shelf water into the basin by ocean current with mixing or diffusion (Shakhova et al., 2010; Matveeva et al., 2015; Lorenson et al., 2016).

1.6 Objective of the thesis

Global warming affects air temperature, SST, ocean biogeochemistry, sea ice cover, characteristics of water masses and so on. It leads to involve dissolved CH₄ distribution in seawater especially in the polar regions where are well-known the most sensitive to climate change. Atmospheric CH₄ concentration continues increasing over the past 150 years (Etheridge et al., 1992) due to increasing amount of CH₄ entering the atmosphere. Thus, this is a motivation to study CH₄ cycling with combining of physical and biogeochemical factors under climate change in the polar regions.
The sea-air CH$_4$ flux estimations are still large uncertainty, and the contribution of oceanic CH$_4$ production is still poorly understood because of the sparsity of available data in the previous studies. Examination of comprehension of CH$_4$ dynamics in surface seawater and water column is needed to investigate. Improvement of measurements and observations recently aims to enhance the accuracy of CH$_4$ flux estimation. Clarification of spatial distribution features of sea-air CH$_4$ flux with high-resolution data is one of the main purposes of this study to reduce these uncertainties. Almost previous studies focused on the influence of biochemical factors on dissolved CH$_4$ distribution in seawater than physical factors. Combining effects of physical and biogeochemical factors to investigate CH$_4$ distribution and sea-air CH$_4$ flux in the polar regions is different from the previous studies. I would like to know and understand how these factors control dissolved CH$_4$ distribution in seawater.

We conducted new continuous measurement of CH$_4$ in the eastern Southern Ocean in austral summer 2012-2013, and in the Arctic Ocean in summer 2015. Also, discrete samples of dissolved CH$_4$ were taken in the same cruise in 2015. Another Arctic expedition cruise conducted in the Arctic Ocean and extended to the northern Arctic Ocean in August 2016. Sampling, results, and discussion in each region are shown in each chapter with distinct factor impacting to dissolved CH$_4$.

In this thesis, contents include: General introduction of CH$_4$ is shown in Chapter 1. Chapter 2: Measurement system, new continuous measurement system coupling with an equilibrator and Gas chromatography - Isotope Ratios Mass Spectrometer, is used to detect dissolved CH$_4$ in seawater. Consideration of controlling factors impact to dissolved CH$_4$ distribution with high-resolution data in the Southern Ocean which is shown in Chapter 3. Influence of a warm-core eddy on CH$_4$ distribution in the Arctic Ocean is reported in Chapter 4. CH$_4$ distribution in the Arctic Ocean in the sea ice cover is displayed in Chapter 5. Finally, General Conclusions is described in Chapter 6.
CHAPTER 2: METHODS

In this chapter, I describe the continuous underway measurement of oceanic CH$_4$ coupling with an equilibrator and Gas Chromatography (GC) measurement of CH$_4$ and N$_2$O. In addition, measurement of DMS/DMSP is also shown by GC equipped with Flame Photometric Detector (FPD).

2.1 Cavity-Ring Down Spectroscopy system (CRDS)

In this study, Cavity Ring-Down Spectroscopy (CRDS) system coupling with an equilibrator is using for detecting dissolved CH$_4$ in seawater.

CRDS is a highly sensitive technique using an optical cavity to measure absorption on the order of parts per million. Basing on tunable light sources were chosen, the spectroscopy and kinetics of chemicals can be detected. A laser is used as a device that emits light through a process of optical amplification and attenuation through reflected mirrors. When molecule gas is present, the rotational vibration modes provide additional loss mechanism and the ring-down times get shorter and is continuously repeated (~100 times per second). The loss of light is leakage through the mirrors produced a signal, the light intensity inside the cavity steady leaks out and decayed to zero in an exponential shape. This decay, or "ring-down", is measured in real-time by a photo-detector. The concentration of any gaseous species can be determined by measuring the strength of this absorption. The final concentration data is particularly robust because it is derived from the difference between these ring down times and is therefore independent of laser intensity fluctuations or absolute laser power. The ring-down profiles are transformed into an absorption curve with a line shape and are used to calculate the gas concentration. The gas concentration is determined by a multi-parameter fit to line-shape and is proportional to the area under the curve (Fig. 2.1) (https://www.picarro.com).

Light intensity is a function of time in CRDS system that has a resonant absorbance. The absorbance (A) can be calculated by the equation:

$$A = \ln \left( \frac{I_0}{I} \right) = \sigma L_{abs} N$$

where: A: absorbance; $I_0$: initial light intensity; I: transmitted light intensity; $\sigma$: absorption across section; $L_{abs}$: path length of light through the absorber; N: number density of absorber molecules.
If the loss process for light is leakage only through the mirrors, the ring down is characterized by:

\[ I = I_0 \exp \left( -\frac{t}{\tau_o} \right) \]

with \( \tau_o = \frac{\tau_r}{2(1-R)} = \frac{L_{opt}}{c(1-R)} \)

where: \( \tau_r \): roundtrip time for light in the cavity; \( R \): mirror reflectivity; \( L_{opt} \): a distance between two mirrors; \( c \): speed of light; \( \tau_o \): 1/e decay time of the light (ring down lifetime).

Recently, CRDS is installed at atmospheric chemistry, is used for measuring concentrations of CH₄, CO₂, N₂O, NH₃ and water vapor. By combination with an equilibrator in order to extract CH₄ and CO₂ in seawater and is detected by CRDS.

Oceanic and atmospheric CH₄ and CO₂ measurements were made quasi-continuously onboard R/V Mirai (Japan Agency for Marine-Earth Science and Technology). Underway measurements of CH₄ and CO₂ mixing ratios in dry air equilibrated with seawater (\( x_{CH_4}^{eq} \)) and ambient air (\( x_{CH_4}^{air} \)) were obtained with a system consisting of a cavity ring-down spectroscopy analyzer (CRDS G2301, Picarro, Inc., California, USA). A shower-head type equilibrator has been used for measurement of the partial pressure of CO₂ in seawater and overlying air since the late 1960s (Kortzinger et al. 2000; Yoshikawa-Inoue 2000; Yoshikawa-Inoue & Ishii 2005).

Seawater was pumped from a water inlet ~5 m below the sea surface at the bow of the ship to an onboard laboratory for measurement of CO₂ and CH₄, salinity, dissolved oxygen and fluorescence. Sampled seawater was continuously introduced into the equilibrator at 10 L/min. Seawater temperature in the equilibrator was measured continuously with a PT-100 sensor. During the cruise, the increase of water temperature from the water inlet to the equilibrator was between 0.1 °C (at low latitudes) and 0.4 °C (at high latitudes). Air equilibrated with seawater was drawn continuously from the outlet of the equilibrator, then flowed into the CRDS analyzers (100 mL/min), and was then returned to the equilibrator. Sample air was circulated within a closed loop during measurements of oceanic CO₂ and CH₄. To avoid band broadening effects caused by water vapor (Bates et al. 1996; Nara et al. 2012), water vapor was removed from the sample air by two electric dehumidifiers that use the Peltier effect, Nafion tubing (Perma Pure LLC, NJ, USA), and a chemical desiccant column (Mg(ClO₄)₂). Equilibration pressure was assumed to be atmospheric pressure because the seawater inlet in the onboard laboratory was at atmospheric pressure.

The CRDS analyzer was calibrated daily with three CH₄ and CO₂ reference gases (1606.2, 1876.5, and 2075.1 ppb for CH₄; 249.23, 380.78, and 444.14 ppm for CO₂); the CH₄ data are
traceable to the World Meteorological Organization CH$_4$ mole fraction scale (Dlugokencky et al., 2005; Tsuboi et al., 2016). The CRDS analyzer produced about 100 digital analyses per minute from which we calculated and used one-minute means. We discarded data recorded for at least 30 min immediately after the changes in flow patterns during measurements of reference gases and ambient air. Based on replicated measurements of a sample gas in the cylinder, the precision of the analyses (±1σ) was estimated to be better than 0.1 ppm and 2 ppb for CO$_2$ and CH$_4$, respectively.

Although both CO$_2$ and CH$_4$ were measured simultaneously during the cruise, I focused in this study on the CH$_4$ distribution, the factors controlling the CH$_4$ distribution, and the sea–air flux of CH$_4$. CH$_4$ concentrations in surface seawater ($C_w$) and the mixing ratio in dry air of CH$_4$ equilibrated with surface seawater ($x_{CH_4}^{sw}$) were calculated by using the temperature and salinity dependence of CH$_4$ solubility in seawater (Wiesenburg and Guinasso, 1979) and the barometric pressure at the sea surface ($P_{bar}$). The partial pressure of CH$_4$ in surface seawater ($p_{CH_4}^{sw}$) was calculated as

$$p_{CH_4}^{sw} = x_{CH_4}^{sw}(P_{bar} - W)$$

where $W$ is water vapor pressure equilibrated with surface seawater.

Similar to $C_w$ calculations, CH$_4$ concentrations in the ambient atmosphere ($C_a$) and the mixing ratios of CH$_4$ in the ambient air ($x_{CH_4}^a$) were calculated by using equilibrium temperature and salinity dependence of equilibirum CH$_4$ solubility upper the surface seawater. The partial pressure of CH$_4$ upper the surface seawater ($p_{CH_4}^a$) was calculated as

$$p_{CH_4}^a = x_{CH_4}^a(P_{bar} - W)$$

2.2 Gas chromatography: Isotope Ratios Mass Spectrometer (GC-IRMS)

2.2.1 Seawater sampling of CH$_4$ and N$_2$O

We took seawater samples during the cruise from a Niskin bottle attached to a conductivity-temperature-depth (CTD) rosette at a certain depth. Seawater was poured continuously into a 120 mL glass vial and had overflowed until at least 240 mL for avoiding contamination in the ambient air. After subsampling, 0.5-mL of a saturated solution of mercuric chloride (HgCl$_2$) was added to prevent biological activity in the vials. Then bottles were immediately sealed using butyl-rubber caps and aluminum caps with at least no headspace. The samples were then stored at about 4°C in the cooling room for later GC analysis in the
laboratory on land. These samples had been measured for dissolved CH\textsubscript{4} and N\textsubscript{2}O in seawater by a gas chromatography - isotope ratios mass spectrometer (GC-IRMS).

### 2.2.2 Gas chromatography: Isotope Ratios Mass Spectrometer (GC-IRMS)

Both mixing ratios and stable isotopic composition of CH\textsubscript{4} and N\textsubscript{2}O of seawater samples were determined by Gas Chromatography - Isotope Ratios Mass Spectrometer (GC-IRMS). Details of the analytical method we used have been reported by Tsunogai et al. (2000) and Hirota et al. (2009). The analytical system consisted of a purge-and-trap CH\textsubscript{4} and nitrous oxide (N\textsubscript{2}O) extraction unit, a GC (HP6850; Agilent Technologies, Santa Clara, CA, USA), an IRMS (Finnigan MAT 252; Thermo Fisher Scientific, Waltham, MA, USA) with a combustion interface (Combustion III, Thermo Fisher Scientific), a gas dryer (dry ice temperature trap (-79°C)), a liquid N\textsubscript{2} temperature trap and liquid O\textsubscript{2} trap (Figure 2.2). Dissolved CH\textsubscript{4} and N\textsubscript{2}O in the samples was extracted by an ultra-pure helium gas stream (>99.99995%) as a carrier gas with a flow rate of 80 ml/min. CH\textsubscript{4} was separated from other gases such as H\textsubscript{2}O, CO\textsubscript{2}, N\textsubscript{2} and non-condensable gases in seawater sample when going through this system. H\textsubscript{2}O and CO\textsubscript{2} are removed by a chemical trap filled with magnesium perchlorate (Mg(ClO\textsubscript{4})\textsubscript{2}; Wako Pure Chemical Industries, Ltd., Osaka, Japan) and Ascarite II (NaOH-coated silica; Thomas Scientific, Swedesboro, NJ, USA). The gas stream, including CH\textsubscript{4} and N\textsubscript{2}O, was then passed through a dehydration unit (U-shaped stainless steel trap at dry-ice temperature). The extracted CH\textsubscript{4} and N\textsubscript{2}O were collected in different trap and were maintained at -183°C and -195°C using liquid oxygen and liquid nitrogen bath, respectively. The non-condensable gases such as N\textsubscript{2}, O\textsubscript{2}, Ar, and CO could passed through these trap and could be released into the atmosphere. Trace gases, including N\textsubscript{2}O and CH\textsubscript{4}, were trapped in a cryotrap (Silicosteel tubing packed with Porapak-Q) at liquid-oxygen temperature. The concentrated gases were released from the trap by heating under helium flow and then re-concentrated on the head of a PoraPLOT-Q capillary column (Chrompack, Inc., Raritian, NJ, USA) maintained at liquid-oxygen temperature. Then, the liquid-oxygen trap was removed to release trace gases and introduced into the column of GC that maintained at 30°C. Trace gases were separated by using helium flow rate of 0.69 mL/min, and finally, they were converted to CO\textsubscript{2} by passing over the combustion interface maintaining at 960°C and then carried into a Finnigan MAT 252 for measuring carbon content and carbon isotope. Determining CH\textsubscript{4} and N\textsubscript{2}O were individually indicated by the retention time at 390 s and 530 s, respectively. Then, the CO\textsubscript{2} was introduced into mass spectrometer in order to determine δ\textsuperscript{45} and δ\textsuperscript{46} of CO\textsubscript{2}. The δ\textsuperscript{13} values of CH\textsubscript{4}
calculated from $\delta^{45}$ and $\delta^{46}$ values of CO$_2$. In contrast, both $\delta^{15}$N$_{N_2O}$ and $\delta^{18}$O$_{N_2O}$ calculated from the $\delta^{45}$ and $\delta^{46}$ values of N$_2O$.

After each single analysis, the column was heated to 120°C at a rate of 5°C/min in order to remove contaminants from the column. During the time, seawater sample in the purging bottle was run out via the water vent. The purging bottle, water transfer line was washed out with pure water and flushed using carrier gas in preparation for the next sample. Each sample analysis took about 50 min.

2.3 Calculation of CH$_4$ concentration, saturation, and sea-air flux

2.3.1 Calculation of CH$_4$ concentration for CRDS system

The solubility of CH$_4$ is calculated by the method of Wanninkhof (2014) as:

$$\ln \beta = A1 + A2 \left(\frac{100}{T}\right) + A3 \ln \left(\frac{T}{100}\right) + S \left[(B1 + B2\left(\frac{T}{100}\right) + B3 \left(\frac{T}{100}\right)^2\right]$$

where $\beta$ is the dimensionless Bunsen coefficient; $K_o$ is the solubility expressed in mol L$^{-1}$ atm$^{-1}$. T is sea water temperature in Kelvin and S is salinity in ‰. A1, A2, A3, B1, B2, and B3 are constant values which are shown in Table 2.1.

Dissolved concentration of CH$_4$ in seawater ($C_w$) is calculated as

$$C_w = K_o \times pCH^{SW}_4$$

(2)

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<th>Table 2.1 Coefficients for temperature and salinity dependence of solubilities of CH$_4$ (Wanninkhof, 2014).</th>
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<td><strong>CH$_4$</strong></td>
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<td>CH$_4$</td>
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2.3.2 Saturation and Sea-air flux calculation

The saturation ratios (SR) of dissolved CH$_4$, which is the ratio of the $C_w$ to the CH$_4$ concentration in seawater equilibrated with ambient air ($C_a$), is given by:

$$SR(\%) = \frac{C_w}{C_a} \times 100$$

(3)
SR < 100% indicates water that is undersaturated relative to the atmosphere, and SR > 100% indicates supersaturation; SR is not affected by barometric pressure. The sea–air flux of CH₄ (F) was calculated as

\[ F = k \times K_o \times (pCH_4^{sw} - pCH_4^{air}) = k \times (C_w - C_a), \]  

(4)

where \( K_o \) is CH₄ solubility in seawater and \( k \) is the gas transfer piston velocity calculated by the method of Wanninkhof (2014) as

\[ k = 0.251 \langle U_{10}^2 \rangle (Sc/660)^{-0.5} \]  

(5)

Here, \( \langle U_{10}^2 \rangle \) is wind speed 10 m above the sea surface, and Sc is the Schmidt number of CH₄ in seawater.

Total CH₄ emissions in the Southern Ocean were calculated as

\[ \text{Total CH}_4 \text{ emissions} = \sum_{i=1}^{n} (F_i \times SA_i) \]  

(6)

where subscript \( i \) is grid number, and SA is the surface area within a grid where the sea surface is free of sea ice. In this study, I assumed no CH₄ exchange across the air-sea interface where there is sea ice.

2.5 Gas chromatography: Flame Photometer Detector (GC-FPD)

2.5.1 Seawater sampling of DMS/DMSP

We took DMS samples during the cruise from a Niskin bottle attached to CTD rosette from at a certain depth. Seawater was directly passed through a 47 mm GF/F filter (pore size 0.7 μm, Manufactured by Whatman) via a tubing, which is fixed by filter holder (PP-47 type, Advantech), into a 30 mL brown glass vial without contacting to the air. Then bottles were sealed by using rubber caps and aluminum caps. Another two DMSP samples were collected in each 30 mL brown glass vial without filtration. Then in the laboratory, 300 mL of magnetic filter funnel using a GF/F wetter filter with a small amount of Mili-Q water, gravity filtration was carried out and took 4 mL of dissolved DMSP (DMSPd) comparing to a testing-standard volume which was prepared. 0.5-mL of 5M HCl (hydrochloric acid) was added into sub-sample of 4 mL seawater by using 1000 μL micropipette to prevent a transformation of DMSP to DMS and biological activities. These bottles were sealed with a rubber cap and aluminum cap and stored in a dark container. For total DMSPt (DMSPt) sample, 8 mL seawater was sucked out and added into 10 mL brown vial by using 5000 μL micropipette. Then 1 mL of 5M HCl was
added into sub-sample of 8 mL by using 1000 μL micropipette and was sealed with a rubber cap and aluminum cap and stored in a dark container.

2.5.2 Gas chromatography: by Flame Photometer Detector (GC-FPD)

DMS and DMSP concentrations were measured by Gas Chromatography (GC-2014, Shimazu) equipped with Flame Photometer Detection (FPD). GC-FPD is a technique used to analyze sulfur or phosphorus compounds. FPD is a type of detector which is used to separate components by burning with hydrogen flame and emitted specific wavelength for phosphorus and sulfur. Thus, GC-FPD is known useful for DMS measurement.

Before using measurement system, the lines were needed to purify by flowing Helium carrier gas through connecting line and GC, and the column was heated to 140℃ for a few hours. DMS and DMSP standard solutions need to calibrate to the amount of signal intensity. 4 mL of NaOH 5M was added to 30 mL of DMSP standard solution of each concentration and then leave it in a refrigerator at 4℃ for a day. During that time, DMSP was converted to DMS, show the correlation between them with a slope of 3124.3 (R^2 = 0.997) Fig. 2.4. The range of detection of DMS concentrations is from 0-32.3 (nmol L^-1).

Before doing an experiment, 1 ml and 2 ml of alkalinity (NaOH) 5M was added into DMSP bottles in order to permit the cleavage of DMSP into gaseous DMS. Then, bottles were shaken and stored at 4℃ for at least 12 hours to complete the cleavage before analysis. For DMS samples, 30 mL of filtered seawater was transferred to glass purging bottle from syringe connected directly to sample. The dissolve DMS was extracted from sample water and transformed into the gas phase by purging with pure nitrogen gas for 12 minutes. The extracted DMS and water vapor were needed to separate them. Water vapor was trapped at 8 mm glass U-shape tube (SIBATA) in the 99.99% ethanol with dry-ice bath (-78℃). The extracted DMS was passed through H_2O trap and was concentrated in another glass U-shape tube with chemical substance TENAX TA 60/80 mesh for absorbing DMS in a dry ice-ethanol bath (-78℃). After the extraction completed (about 14 minutes 30 seconds), the liquid in the purging bottle is left via water vent. Thereafter, the DMS gas trapped in the U tube was warmed with the boiling water of about 95-100℃ (hot trap) and released gas was introduced into a GC equipped with FPD detector for separation and detection. Sulfur compounds including DMS were detected by FPD (see Fig. 2.5).

Seawater samples for measuring DMS concentrations were measured onboard as soon as possible after filtering treatment. However, seawater samples for measuring DMSP whenever
on board or in the laboratory after adding acid solution and storing in a dark place. For measuring DMSP, it is needed to convert to DMS firstly, and then leaving it in a cool dark place for at least a half-day, and measured it. Due to chemical converting treatment of DMSP, it is often measured on land.

2.6 Calculations of biogeochemical parameters

2.6.1 Apparent Oxygen Utilization (AOU)

AOU is the difference between the measured dissolved oxygen concentration and its equilibrium saturation concentration in water with the same physical and chemical properties. AOU is defined as:

\[ \text{AOU} = [O_2]_{sat} - [O_2]_{obs} \]

\([O_2]_{sat}\): the value of oxygen in the water in equilibrium with the atmosphere at temperature and salinity of the water. It is called saturation; it implies that all water is in equilibrium with the atmosphere. \([O_2]_{obs}\): is dissolved oxygen observed in the water sample. Biological activities act to change the ambient of oxygen concentration; it leads to change in AOU. Primary production releases oxygen and increases its concentration, while respiration consumes and decrease its concentration. In shallow water, the water column is generally in contact with the atmosphere, so oxygen concentration is typically close to saturation, or AOU value is low. In deep water, water can be out of contact with the atmosphere for long periods of time and large AOU is possible (Garcia et al., 2006).

2.6.2 Fixed nitrogen (N**)

N** is a modification of N*, a parameter defined by Gruber and Sarmiento (1997) (Codispoti et al., 2005a):

\[ N^{**} = [\text{NO}_3^-] + [\text{NO}_2^-] + [\text{NH}_4^+] - 16[\text{PO}_4^{3-}] + 2.9 \]

This parameter estimates the impact of in situ fixed nitrogen additions and removals on water masses. N** includes ammonium concentrations because of the high ammonium values (Codispoti et al., 2005a). N** is a quasi-conservative tracer, the global mean ratio of 106:16:1 between carbon, nitrogen, and phosphorus (C:N:P). N** is about zero if the Redfield ratio is retained, a negative N** value indicates a deficit of dissolved inorganic nitrogen (due to denitrification), while a positive value indicates N fixation (Redfield, 1942; Gruber and Sarmiento, 1997).
Nishino et al. (2005) define for N** that differs 0.1 µmol kg⁻¹. Pacific water enters the Arctic tend to have negative values due to the conversion of fixed-nitrogen to free nitrogen (N₂) that process enhanced in low oxygen water and sediments. Atlantic water has a positive value because of net nitrogen fixation (Codispoti et al., 2005b). Because of the influence of microbial processes in shelf sediments, it causes a reduction in N** (Devol et al., 1997).
Fig. 2.1. Schematic of CRDS analyzer with a laser source, reflected mirrors and detector (upper) and profile of a ring down measurement (source: https://www.picarro.com).

Fig. 2.2 Schematic diagram of underway system for measurements of CO$_2$ and CH$_4$, consisting of a CRDS analyzer and a shower-head-type equilibrator.
Fig. 2.3 Schematic diagram of a system using for CH₄ and N₂O analysis. 6V: six-port two-position Valco valve; STD: gas standard; GC: gas chromatography; MFC: mass flow controller.

Fig. 2.4 The linear relationship between roots of signal intensity and DMS concentration of 30-mL DMSP standard was carried in the laboratory. Solid line shows the linear relationship between DMS concentration and signal intensity: $y = 3124.3x$ ($R^2 = 0.997$).
Fig. 2.5 Schematic diagram of the system using for DMSP analysis. MFC: mass flow controller; ECU: Electronics Cooling Unit; 2PV: two-port valve; MFM: mass flow meter; GC-FPD: gas chromatography equipped with Flame Photometric Detector.
CHAPTER 3:
HIGH-RESOLUTION METHANE EMISSIONS
IN THE SOUTHERN OCEAN

3.1 CH₄ distribution in the Southern Ocean

There are some works that have investigated CH₄ concentration in the Southern Ocean (Lagmontag et al., 1973; Bates et al., 1996; Tilbrook and Karl, 1994; Heeschen et al., 2004; Yoshida et al., 2011). Dissolved CH₄ concentrations are supersaturated but both supersaturation and undersaturation are known in the extratropics (Kelly and Jeffrey, 2002) and at high latitudes (Bates et al., 1996; Yoshida et al., 2011). The main factors that control CH₄ supersaturation in tropical and extratropical regions are equatorial upwelling and seasonal variations of sea surface temperature (SST), respectively (Bates et al., 1996). In the pelagic zone, bacterial CH₄ is released from the digestive tracts of zooplankton and from sinking organic particles; CH₄ is removed from ocean waters by microbial oxidation and by sea–air flux (Grunwald et al., 2009). In productive coastal areas, large amounts of CH₄ are produced by methanogenesis in buried sediment layers, which account in part for the high contribution of coastal areas and estuaries to the sea–air flux of CH₄ (Bange et al., 1994).

The CH₄ is produced by microbial methanogenesis in anaerobic environments and by bacteria in organic particles or in the gut of zooplankton (Karl and Tilbrook, 1994). CH₄ production from methyl phosphate decomposition in the aerobic environment has been reported (Karl, 2008). Recently, observation of a release CH₄ from sinking particles into the water column by measuring of dissolved CH₄ concentration and δ¹³C-CH₄ (Sasakawa et al., 2008). Methanogens have been shown to be zooplankton-species-specific (de Angelis and Lee, 1994), which contributes to the lack of a consistent correlation between CH₄ concentrations in seawater and commonly measured biological parameters. Burke et al. (1983) reported weak correlations between CH₄ concentrations and particulate and biological parameters in the eastern tropical North Pacific and that the CH₄ distribution there was largely controlled by physical oceanographic processes.

In the surface water in the Southern Ocean has been reported that undersaturated CH₄ with respecting to atmospheric CH₄ and a small sink to the atmosphere (Tilbrook and Karl, 1994). Undersaturation of CH₄ deep in the water column in the Arctic Ocean is a result of microbial oxidation (Rehder et al., 1999) and is consistent with the maximum seawater
temperature in the core of Warm Deep Water (Heeschen et al., 2004). In the Southern Ocean, low CH$_4$ in surface water is a consequence of entrainment by surface water of deep water depleted in CH$_4$ (Yoshida et al., 2011) because of its low content of organic particles (Fischer et al., 1988), upwelling of old deep water (Heeschen et al., 2004, Rehder et al., 1999), or both.

The Southern Ocean is one of the most biologically productive oceanic regions in the world; it is characterized by high biomasses of zooplankton, Antarctic krill, and salps (Knox, 2007), all of which produce large amounts of CH$_4$. Although some researchers have measured CH$_4$ concentrations in the Southern Ocean (Lagmontag et al., 1973; Bates et al., 1996; Tilbrook and Karl, 1994; Heeschen et al., 2004; Yoshida et al., 2011), accurate assessment of the sea–air flux of CH$_4$ has been limited by the sparsity of available data. This study aims to clarify the spatial distribution of the sea–air flux of CH$_4$ in the Southern Ocean and thus to reduce the uncertainties in estimations of the ocean as a source of atmospheric CH$_4$. Here, I present the distribution of the sea–air flux of oceanic CH$_4$ along the course of a scientific cruise in the Pacific and Indian sectors of the Southern Ocean during the 2012/13 austral summer; I use SR and AOU correlation to examine the climatological flux of CH$_4$ from the entire Southern Ocean south of 50°S during the austral summer.

3.2 Water masses in the Southern Ocean

In the Southern Ocean, major oceanic fronts separate water masses with different physical and biogeochemical properties (Sarmiento et al., 2004). The oceanic front is a boundary between two distinct water masses, moves around Antarctica. It was defined by SST and sea surface salinity (SSS). These are the Sub-Tropical Front (STF), Sub-Antarctic Front (SAF), Polar Front (PF), Southern Antarctic Circumpolar Current Front (SACCF), Southern limit of Upper Circumpolar Deep Water or Southern Boundary (SBDY), and Antarctic Slope Front (ASF) (Orsi et al., 1995; Rintoul et al., 1997; Rintoul and Bullister, 1999; Yaremchuk et al., 2001; Ainley and Jacobs, 1981). The Sub-Antarctic Zone (SAZ) locates between STF and SAF, the Polar Frontal Zone (PFZ) between SAF and PF, the Antarctic Zone (AZ) between PF and SACCF, the Southern Zone (SZ) between SACCF and SBDY, and the south of SBDY (SSBDY).

A major dynamic feature of the Southern Ocean is the Antarctic Circumpolar Current (ACC), which flows eastward around Antarctica and mixes with the various water masses along its path (Callahan, 1972; Georgi, 1981). The most voluminous water mass is Circumpolar Deep Water (CDW), which is carried around Antarctica by the ACC (Whitworth and Nowlin,
Near Antarctica, CDW moves upward through the water column from north to south, approximately along the equal density surface, and mixes at the shelf break with shelf waters (Locarnini, 1994).

3.3 Regional Setting

Oceanic and atmospheric CH$_4$ and CO$_2$ measurements were made quasi-continuously onboard R/V Mirai (Japan Agency for Marine-Earth Science and Technology) during the Pacific and Indian sectors of scientific cruise MR12-05 (legs 2 and 3) in the Southern Ocean from late November 2012 to mid-February 2013 (Fig. 3.1). Fig. 3.1 depicts the distribution of oceanic fronts drawn on the basis of Orsi et al. (1995). Besides, I also compare CH$_4$ to another measurement of biochemical variables to investigate the controlling factors to CH$_4$ distribution. Along the cruise track, we determined the geographical position of each oceanic front on the basis of vertical profiles of temperature and salinity (Orsi et al., 1995; Rintoul et al., 1997; Rintoul and Bullister, 1999; Yaremchuk et al., 2001), SST, and SSS (Chaigneau and Morrow, 2002). The cruise included a zonal transect along the World Ocean Circulation Experiment Hydrographic Program line S4 and four meridional transects.

Along 140°E, the STF is the boundary between warm, salty subtropical water and cool, fresh sub-Antarctic water, which is located at 44°S. The SAF is recognized by a steep horizontal gradient of SST occurred around 54°S, which is the northern edge of the eastward-flowing Antarctic Circumpolar Current. The PF is characterized by a steep temperature gradient of SST and the northern limit of minimum-temperature water with temperatures of less than 2°C near a depth of 200 m, located at 59°S. The SACCF coincides with the southern limit of maximum temperature water over 1.8°C (Orsi et al., 1995), located around 62°S. SBDY is located at 63.5°S, where temperature maximum is 1.5°C (Orsi et al., 1995).

3.4 Results and Discussion

3.4.1 Spatial distribution of dissolved CH$_4$ in seawater

Calculated CH$_4$ concentration varies from 2.1-3.6 nmol kg$^{-1}$ with an averaged value of 3.1 nmol kg$^{-1}$ (Fig. 3.2) from CRDS system during the cruise. CH$_4$ concentrations tend to be increased toward the Antarctica Continent while dissolved CH$_4$ concentration is generally low in tropical regions. Concurrently, sea surface CH$_4$ concentrations by using GC measurements ranged 2.9–4.2 nmol kg$^{-1}$ (Fig. 3.3). The degree of saturation of dissolved CH$_4$ (SR) was
calculated from the observed CH$_4$ concentration ($C_w$) and the concentration of CH$_4$ in water equilibrated with ambient air ($C_a$, $C_a$ is observed during the cruise). The overall SR in the sea surface ranged from 85-142\% (Fig. 3.4), with an average CH$_4$ saturation was 104\%. The estimated values were mostly within the ranges reported in the previous studies.

### 3.4.2 Comparison of $C_w$ determined by the underway system and by GC-IRMS

$C_w$ determined by the underway system ranged from 2.1 to 3.6 nmol kg$^{-1}$ (mean = 3.1 nmol kg$^{-1}$) during leg 2 of cruise MR12-05 (Fig. 3.1). I used reduced major axis (RMA) regression to compare $C_w$ values determined by the underway system with those determined for discrete water samples by GC-IRMS. RMA analysis gave a regression line with a slope of 1.0 ± 0.1 ($r^2 = 0.84$, $n = 39$), which indicates that, within the precision of the analyses, the variations in $C_w$ determined by the underway system were equivalent to those of the purge-and-trap technique we used for our discrete water samples (Reeburgh, 2007). A moderately large regression line intercept (–0.5 ± 0.2), indicates that the GC analyses gave $C_w$ values that were ~0.5 nmol kg$^{-1}$ greater than those of the CRDS analyses. Similar differences were reported by Bates et al. (1996) who also used the underway system: they reported lower SR values for the underway system than those from comparable discrete water samples reported by Watanabe et al. (1995). Forster et al. (2009) also reported that equilibrated CH$_4$ concentrations measured underway were significantly lower than those obtained from rosette samples.

To allow further and more detailed discussion of the differences between the results of these two methods of analysis, I need to reconsider the need for collection of discrete seawater samples, the methods employed for preservation of such samples, GC-IRMS analysis of seawater samples, and equilibrium in the equilibrator (SCOR WG #143, 2014, https://portal.geomar.de/web/geomar-wg-143). The mole-fraction scale of reference gases used and the natural variability of oceanic CH$_4$ must also be taken into account. Further discussion of the consistency of the results of the two methods is beyond the scope of this paper.

### 3.4.3 Mixing ratios of atmospheric CH$_4$

Temporal variation of atmospheric CH$_4$ in the Southern Hemisphere was examined to confirm that the atmospheric CH$_4$ mixing ratios measured by the CRDS analyzer were accurate (Fig. 3.6). During the cruise, the mean of atmospheric xCH$_4^{\text{air}}$ was 1775.9 ± 5.4 ppb ($n = 33$) in late November 2012, 1767.2 ± 5.4 ppb ($n = 321$) in December 2012, 1755.7 ± 2.0 ppb ($n = 304$) in January 2013, and 1751.0 ± 1.5 ppb ($n = 150$) in early February 2013, and showed the same seasonal variations as reported for the Southern Hemisphere by Dlugokencky et al. (1994).
Mean values in December 2012 and January 2013 agreed well (within 5 ppb) with monthly means at Cape Grim (40.68°S, 144.69°E), Tasmania, and at the South Pole, on the basis of data from the NOAA/ESRL network (http://www.esrl.noaa.gov/gmd/ccgg/trends_ch4/).

3.4.4 Meridional distribution of CH₄ in surface seawater

The meridional distribution of pCH₄sw between New Zealand and the SBDY (Fig. 3.7) showed a few pCH₄sw peaks of up to 3.4 µatm and an SR range from 120% to 185% in the coastal area off New Zealand. These peaks can be attributed in part to large amounts of CH₄ that are produced by methanogenesis in buried sediment layers in productive coastal areas (Grunwald et al., 2009; Hovland et al., 1993; Scranton and McShane, 1991). CH₄ inputs from riverine and groundwater discharge can also contribute to CH₄ supersaturation in coastal areas (Bugna et al., 1996; Kim and Hwang, 2002; Reeburgh, 2007). In surface seawater off the New Zealand coast, strong pCH₄sw peaks are accompanied by lower water density (lower SSS), which likely reflects the input of fresh water with high CH₄.

In the open ocean area from the STF to the SBDY (Fig. 3.7), pCH₄sw decreased slightly and monotonously to the south and SR decreased from 119% to 100%; both of these results agree well with those of earlier studies (see Table 3.1; Bates et al., 1996; Kelly and Jeffrey, 2002). Atmospheric CH₄ has increased by 180 ppb (about 10%) between 1984 and 2012, although the rate of increase was slower between 1999 and 2006 (Dalsøren et al., 2016; McNorton et al., 2016). The fairly constant SR over these few decades suggests parallel increases of pCH₄sw and pCH₄air. South of the SBDY (63.5°S), pCH₄sw decreased considerably along with decreases in SST and chlorophyll-a concentration and an increase in AOU. The lowest value of SR that we observed (85%) was in this region.

South of the STF, pCH₄sw changed little (Fig. 3.7), but there were steep changes in SST and SSS at each of the other fronts. Because CH₄ solubility is a function of SST and SSS (Wiesenburg and Guinasso, 1979), the relatively constant pCH₄sw indicates that there must have been changes in C_w at each front. According to Wiesenburg and Guinasso (1979; their equation 7), CH₄ solubility decreases by 2.3% for each unit increase in SST above 10 °C at constant SSS (34), and by 0.8% for each unit increase in SSS from 34 at constant SST (10 °C). The decreases of SST and SSS to the south caused large increases of C_w to the south. In the region between the PF and the SBDY, C_w tended to be high, suggesting enhancement of biogenic CH₄ production (Heeschen et al., 2004), lower rates of CH₄ oxidation and CH₄ flux between the sea and overlying air, or both.
The meridional variations of pCH$_4^{sw}$ during the sections of the cruise sailing toward and away from southern Tasmania, and during the northbound section sailing toward Fremantle (Figs. 3.1 and 3.7 to 3.10), were similar to those between the STF and the SBDY between New Zealand and Antarctica (Fig. 3.7). During the northbound sailing to Tasmania, pCH$_4^{sw}$ varied considerably between 1.8 and 2.9 $\mu$atm north of the SAF. Strong pCH$_4^{sw}$ peaks that continued over several tens of kilometers coincided with increases in chlorophyll-a concentration. However, about one week after the northbound sailing toward Tasmania we found no strong peaks of pCH$_4^{sw}$ at the same geographical positions (Fig. 3.9). During the northbound sailing to Fremantle, pCH$_4^{sw}$ north of the STF also varied considerably, from 1.8 to 2.7 $\mu$atm, but without correlation with chlorophyll-a concentration, SST, or SSS (Fig. 3.9). Thus, it appears that none of the other quantities I determined in this study can be reliably used to predict strong peaks of pCH$_4^{sw}$ north of the STF.

The minimum pCH$_4^{sw}$ we observed was over the Kerguelen Plateau, where it corresponded to local variations of other parameters: a decrease in SST, a slightly positive AOU (5 $\mu$mol kg$^{-1}$), and elevated chl-$a$ concentration (Fig. 3.10). Gille et al. (2014) reported that cold SSTs in the Kerguelen region correlate with high wind speeds and that wind-mixing of the upper ocean there resulted in entrainment of cold water into the mixed layer and euphotic zone. Mashayek et al. (2017) also identified spatiotemporal changes of mixing of waters in a shallow region of the Southern Ocean by using trifluoromethyl sulfur pentafluoride (CF$_3$SF$_5$) as a passive chemical tracer. In the Southern Ocean, strong vertical mixing is induced by near-surface westerly winds that cause convergent flow at intermediate depths; such mixing partially offsets upwelling (Marshall and Speer, 2012). The fluxes of greenhouse gases between air and sea and those in the water column are affected not only by physical processes, but also by the availability of organic matter and oxygen (Codispoti et al., 2001). CH$_4$ is formed mainly by methanogens (Wuebbles and Hayboe, 2002) during anaerobic degradation of organic matter or by the transformation of methyl compounds by methylotrophs (Damm et al., 2008), whereas CH$_4$ consumption occurs as a result of aerobic methanotrophy (Hanson and Hanson, 1996). In this region, vertical mixing has been reported to support the development of chlorophyll-a blooms (Gille et al., 2014) and high AOU values. AOU is respiration in the ocean interior (without contact with the atmosphere), where lower concentrations of CH$_4$ would be expected because of its removal by oxidation. Positive AOU values in surface seawater suggest that air-sea exchange of O$_2$ and O$_2$ production due to photosynthesis by phytoplankton were too slow to establish equilibrium after or during vertical mixing. Because maximum CH$_4$ concentrations at high latitudes south of the PF are in surface waters and decrease with depth (therefore there
are no subsurface CH$_4$ maxima) (Yoshida et al., 2011), I would expect a negative relationship between pCH$_4^{\text{sw}}$ and AOU.

### 3.4.5 Zonal distribution of CH$_4$ in surface seawater at high latitudes

The pCH$_4^{\text{air}}$ at latitudes south of 60°S (Fig. 3.11) decreased westward, which was a response to seasonal variations in atmospheric CH$_4$ and decreases in barometric pressure. As noted above (see discussion of Fig. 3.6), pCH$_4^{\text{sw}}$ east of 140°E decreased considerably, along with decreases in SST and chlorophyll-$a$ and increases in AOU (Fig. 3.6). Holm-Hansen et al. (2005) reported that in a relatively shallow area of the Southern Ocean bounded by 145° to 170°E and 62° to 66°S, where the bottom topography is complex, and there are numerous islands, banks, and seamounts, upwelling of deep water creates regions of high-chlorophyll pelagic seawater. In very early December, which is before the onset of strong biological activity, observed positive AOU (41 µmol kg$^{-1}$) and low chlorophyll-$a$ concentrations in this region.

Lowering of pCH$_4^{\text{sw}}$ is to be expected with increasing AOU, as was evident over the Kerguelen Plateau (Fig. 3.10), which is consistent with higher AOU than surrounding (Aoki et al., 2007). Aoki et al. (2007) reported that cyclonic eddies of 100–150 km diameter appear every year in a particular area at around 140°E, and that the properties of the water in the eddies are similar to those of water over the continental slope. Large-scale spatial variability of pCH$_4^{\text{sw}}$ might be caused by physical processes such as upwelling and vertical mixing and subsequent downstream biological production of CH$_4$.

### 3.4.6 CH$_4$ distribution in Coastal area

West of 140°E, surface seawater emitted CH$_4$ to the atmosphere, except at high latitudes along 38°E and 53.5°E (transects 1 (TS1) and 2 (TS2), respectively) where SST was lower than 0 °C and AOU was positive (Fig. 3.12). A broad low-amplitude peak of pCH$_4^{\text{sw}}$ at around 110°E coincided with a region of considerable variability of SSS. The large decrease in SSS there suggests input of meltwater in response to sea-ice retreat, which reduces the density of surface seawater. The resultant shallow stratification can trap organisms in the sunlit (productive) layer. Although phytoplankton do not generate CH$_4$ directly, the high pCH$_4^{\text{sw}}$ there is probably a result of Antarctic krill, zooplankton, or both feeding on phytoplankton and the subsequent microbial methanogenesis (Yoshida et al., 2011).

South of the ASF along 38°E and 53.5°E (at 67.5°S and 64.5°S along coastal TS1 and TS2, respectively), pCH$_4^{\text{sw}}$ decreased toward the continent (Fig. 3.12; Fig. 3.13) within the range from 1.65 to 1.69 µatm. The ASF is a strong horizontal subsurface temperature front.
defined by the 0 °C isotherm (Ainley and Jacobs, 1981) and clearly separates the cold and shelf waters from the modified CDW, which can extend all the way to onto the Antarctic Shelf (Williams et al., 2010). Along 53.5°E (TS2, Fig. 3.13), pCH$_4^{sw}$ also decreased southward, accompanied by an increase in AOU, which is the same pattern as that we observed east of 140°E and over the Kerguelen Plateau. The coastward decrease of pCH$_4^{sw}$ is the opposite trend to that observed in tropical and extratropical regions. In the Antarctica, the physical features are the same, either mixing or upwelling; but the upwelled water is distinct. Upwelling of old CH$_4$-poor water characterized by former biological oxidation (Rehder et al., 1999) and/or by contact with a former atmosphere with low methane content off Antarctica (Heeschen et al., 2004), versus upwelled water in the tropics and subtropics fed by depleted oxygen subsurface water and pontentially contact with organic rich sediments (Reeburgh, 2007).

### 3.5 Estimation of sea-air CH$_4$ fluxes in the entire of the Southern Ocean

The pCH$_4^{sw}$ and pCH$_4^{air}$ data we acquired along the cruise track allowed us to use Eq. (3) to evaluate the sea–air flux of CH$_4$ over a wide area of the Southern Ocean (Fig. 3.14). Calculated flux of CH$_4$ we determined ranged from −3.9 to 8.5 µmol m$^{-2}$ day$^{-1}$ (average 0.19 µmol m$^{-2}$ day$^{-1}$) and was greatest and most variable at lower latitudes, especially off New Zealand. In the pelagic zone between the SAF and SBDY, it ranged from −0.43 to 0.50 µmol m$^{-2}$ d$^{-1}$ and there was CH$_4$ uptake by surface seawater in the area of the Kerguelen Plateau. I observed intermittent strong pCH$_4^{sw}$ peaks north of the SAF and STF (see section 3.4.4) that led to the higher sea-air flux of CH$_4$ there. It is important to examine the triggers of these strong pCH$_4^{sw}$ peaks at lower latitudes in our evaluation of oceanic CH$_4$ flux. In the area south of the SBDY and east of 140°E, our data (Fig. 3.14) show that surface seawater there acts as a net sink for atmospheric CH$_4$.

The CH$_4$ flux data I have determined is limited to the course of cruise MR12-05. To gain a good understanding of the oceanic CH$_4$ cycle throughout the South Pacific and the Southern Ocean, I need a much greater geographic spread of data. This might be achieved by using variables such as SST and chlorophyll-$a$ concentration, which are related to the distribution of SR (and hence to pCH$_4^{sw}$) and are measured remotely over wide areas. If such relationships exist between SR and other oceanographic processes, it would then be relatively simple to interpolate or extrapolate observed SR values across the Southern Ocean, which would allow a more precise evaluation of the sea–air flux of CH$_4$. Biological activity (CH$_4$ production and oxidation), ocean dynamics (lateral flow, vertical mixing, and upwelling), CH$_4$ solubility, and the sea–air flux of CH$_4$ have a major effect on the spatiotemporal variation of SR. Based on the
assumption that these factors are directly or indirectly related to SR, we investigated possible relationships between SR at high latitudes (south of 50°S) and SST, chlorophyll-a, water density, and AOU.

First, we examined the SR–SST relationship south of 50°S (taken to be south of the PF). SR increased dramatically with only slight increases in SST (at around 0 °C) (Fig. 3.15). Although no clear relationship between SR and chlorophyll-a was found, such a relationship may exist within areas much smaller than our study area (Damm et al., 2008; Yoshida et al., 2011). Yoshida et al. (2011) reported a strong relationship between C_w and seawater density in the South Pacific–Southern Ocean region, but this relationship does not hold in regions of low SST. While cruising at high latitudes from December 2012 to February 2013, I noted a possible correlation between pCH_4^sw and AOU, which I investigated further (Fig. 3.16). The resultant analysis of data collected along the cruise track in the open ocean south of 50°S shows that the following linear relationship between SR and AOU applies, at least in the Southern Ocean south of 50°S:

\[
\text{SR} = -0.294 \times \text{AOU} + 100.093 \quad (r^2 = 0.89, n = 1549)
\] (3.1)

I got a good correlation between AOU and SR (Eq. (3.1)). In the subsurface water which is brought upward by vertical mixing, is characterized by positive AOU and low pCH_4^sw (Heeschen et al., 2004). At the sea-air interface, the transfer velocity for gas exchange of oxygen and CH_4 is quite similar, it means that undersaturation due to on the same timescale. The correlation here is also a strong indication for lacking of importance of biological production.

To obtain a map of the distribution of the sea–air flux of CH_4 in the Southern Ocean south of 50°S, we first determined the distribution of SR by applying Eq. (6) to the long-term monthly mean AOU data (1° × 1° grid) for December, January, and February from the World Ocean Atlas (2013). Because monthly mean AOU data for each year are not available, so we estimated a SR distribution based on climatological AOU data. Then, we calculated the monthly mean sea–air flux of CH_4 and total CH_4 emission for the three months (Table 3.2 and Fig. 3.17). The sea–air flux of CH_4 is controlled mainly by C_w – C_a (see Eq. (3)) and wind speed, and total CH_4 emission in the Southern Ocean is controlled by the sea–air flux of CH_4 and the amount of sea-ice coverage. Although the AOU data for each grid cell suggest strong uptake of CH_4 in seawater in December, the area of surface seawater in contact with the atmosphere is small at higher latitudes in December due to sea-ice coverage. Although the AOU data suggest that CH_4 uptake in the Weddell Sea and Ross Sea would be considerable, these areas are largely covered
by sea ice in December. From December to January, total CH$_4$ emission increased by 0.014 Tg yr$^{-1}$ owing to an increase in sea–air flux of CH$_4$ and the retreat of sea ice. Following the retreat of the sea ice, CH$_4$ flux tended to be higher slightly south of the sea ice and the coastal region showed a large negative sea–air flux of CH$_4$ (CH$_4$ uptake). From January to February total net CH$_4$ evasion decreased by 44% (0.02 Tg yr$^{-1}$) while both the area of surface in contact with the ambient air and the wind speed increased. In February, CH$_4$ flux was generally small in the area south of the edge of the sea ice. Surface seawater between 50° and 60°S, which is a region of high wind speed, was a source of atmospheric CH$_4$ from December to February. The CH$_4$ flux obtained from gridded AOU data along the cruise track (south of 50°S) was in the range from −2.4 to 2.1 $\mu$mol m$^{-2}$ d$^{-1}$ (mean 0.08 $\mu$mol m$^{-2}$ d$^{-1}$), which is lower than that obtained from our underway measurements (0.194 $\mu$mol m$^{-2}$ d$^{-1}$); we attribute the difference to the effect of strong winds during the cruise, especially near 50°S. In coastal regions, the higher CH$_4$ fluxes obtained from gridded AOU data might also reflect local variations of AOU and coastal dynamic mechanisms, which may have contributed to these higher fluxes. Thus, there are limitations to the use of Eq. (3.1) to extrapolate CH$_4$ fluxes across the entire Southern Ocean.

South of 50°S, the average CH$_4$ flux in austral summer is 0.024 Tg yr$^{-1}$, which accounts for a minor contribution of oceanic release CH$_4$ to the atmosphere (4–15 Tg yr$^{-1}$, IPCC, 2007). Considering that the area the Southern Ocean south of 50°S represents 13% of the global oceanic area, this efflux seems very small, but we attribute it to the high invasion of CH$_4$ at high latitudes. Although we have treated sea ice as an impermeable barrier to sea–air exchange of CH$_4$ in this study, recent studies suggest that gas exchange through sea ice does occur (Nomura et al., 2010, 2013, 2014). The estimates of CH$_4$ flux derived from the AOU–SR relationship is the main highlight of this study: this relationship can be extrapolated to apply at least to the entire Southern Ocean. To improve predictions of future changes of the global sea–air flux of CH$_4$, more observation data are required in areas where these fluxes are most variable, in particular, in the Southern Ocean in areas of seasonal sea ice coverage, in tropical and extratropical coastal regions, and in marginal seas.

### 3.6 Summary and Conclusion

A CRDS system coupled with a shower-head type equilibrator is used to obtain quasi-continuous underway measurements of the mixing ratio of oceanic CH$_4$ in seawater during legs 2 and 3 of cruise MR12-05 of R/V Mirai in the Southern Ocean from late November 2012 to mid-February 2013. Our pCH$_4^{sw}$ data show that surface seawater was supersaturated with CH$_4$
in the tropics and extratropics, but both super- and undersaturated at high latitudes. Undersaturation occurred in areas where SST was low (<0 °C), AOU was positive (up to 41 µmol kg⁻¹), and chl-a concentrations were low (<0.3 µg L⁻¹), indicating that these areas were affected by upwelling and vertical mixing and limited biological production of CH₄. The SR in our entire dataset ranged from 85% to 185% (average 104 ± 4%). High SR in the north is biased due to coastal vicinity.

To attempt a regional evaluation of the sea–air flux of CH₄ over a wide area of Southern Ocean, beyond the limits imposed by using data only from the course of R/V Mirai, I examined the relationships of SR (hence pCH₄sw) with several other oceanographic variables that are being measured remotely over wide areas. For the area south of the PF (50°S), we identified a strong linear relationship between SR and AOU that indicates that vertical mixing and upwelling are important factors that influence the spatial distribution of oceanic CH₄. On the basis of this linear relationship, the regional climatological distribution of the sea–air flux of CH₄ is calculated in the Southern Ocean south of 50°S for the period from December to February. I estimated emissions of CH₄ from the Southern Ocean to be 0.03 Tg yr⁻¹ in December, 0.04 Tg yr⁻¹ in January, and 0.02 Tg yr⁻¹ in February. Total CH₄ emissions increased from December to January in response to the combined effect of an increase in sea–air flux of CH₄ and retreat of seasonal sea ice. From January to February, total CH₄ emissions decreased because the sea–air flux of CH₄ decreased as a result of declines in both wind speed and the area of sea surface in contact with ambient air (increase in sea ice). Although the effect of CH₄ emissions from the Southern Ocean has limited global impact, our results clearly show climatological variations of the sea–air flux of CH₄ in the Southern Ocean from December to February.
Fig. 3.1 Dash-dotted blue line shows the cruise track of R/V *Mirai* where underway measurements of oceanic CO$_2$ and CH$_4$ were made simultaneously. Red circles show hydrographic stations for measurements of CH$_4$ in discrete water samples. Black solid line shows the oceanic fronts from Orsi et al., (1995), and TS1 and TS2 coastal transects at 38°E and 53.5°E, respectively.

Fig. 3.2 Spatial distribution of methane concentration in surface seawater determined by using CRDS system
Fig. 3.3 Spatial distribution of methane concentration in surface seawater determined by using the GC-IRMS system

Fig. 3.4 Spatial distribution of methane saturation in surface seawater determined by using CRDS system
Fig. 3.5 Plot of CH₄ concentration between CRDS system versus GC system during the cruise track of R/V Mirai (MR15-03).

CRDS = (1.0±0.1)×GC + (-0.5±0.2)  
\[ R^2 = 0.84, \ n = 39 \]

Fig. 3.6 Atmospheric CH₄ mixing ratios measured by CRDS analyzer during the cruise track of R/V Mirai (MR15-03).
Fig. 3.7 Meridional distribution of $p\text{CH}_4^{\text{air}}$, $p\text{CH}_4^{\text{sw}}$, chl-$a$, AOU, SST, SSS, $SR$ along transect from offshore New Zealand to Antarctica (A-B).
Fig. 3.8 Meridional distribution of $p\text{CH}_4^{\text{air}}$, $p\text{CH}_4^{\text{sw}}$, chl-$\alpha$, AOU, SST, SSS, SR from SBDY to SAF during northbound sailing to Tasmania (Leg 2) (C-D).
Fig. 3.9 Meridional distribution of $pCH_4^{\text{air}}$, $pCH_4^{\text{sw}}$, chl-α, AOU, SST, SSS, SR from STF to SBDY during southbound sailing (Leg 3) (E-F).
**Fig. 3.10** Same as in Fig. 3.9 except from SBDY to STF during northbound sailing to Fremantle (Leg 3) (G-H).
Fig. 3.11 Zonal distribution of $pCH_{4}^{air}$, $pCH_{4}^{sw}$, chl-$a$, AOU, SST, SSS, SR south of 60°S (B-C-G).
Fig. 3.12 Meridional distribution of pCH$_{4}^{\text{air}}$, pCH$_{4}^{\text{sw}}$, chl-$\alpha$, AOU, SST, SSS, SR at transect 1 (38°E). An arrow at the bottom indicates the position of the coast.

Fig. 3.13 Meridional distribution of pCH$_{4}^{\text{air}}$, pCH$_{4}^{\text{sw}}$, chl-$\alpha$, AOU, SST, SSS, SR at transect 2 (53.5°E). An arrow at the bottom indicates the position of the coast.
Fig. 3.14 The CH₄ flux along the cruise track (red color indicates CH₄ release, and blue color indicates CH₄ uptake in seawater)
Fig. 3.15 The relationship between CH$_4$ saturation (SR) and SST south of 50°S in the Southern Ocean (n = 1549). Colorful dots indicate for data in water masses in the Southern Ocean.

Fig. 3.16 The relationship between SR and AOU south of 50°S in the Southern Ocean. Solid line shows the linear relationship between SR and AOU: SR = -0.294×AOU + 100.093 ($r^2 = 0.89$, n = 1549). Colorful dots indicate for data in water masses in the Southern Ocean.
Fig. 3.17 Monthly mean sea-air CH$_4$ flux in the Southern Ocean from December to February (from upper panel to bottom panel). White areas are sea ice coverage.
Table 3.1 Comparison of CH₄ saturation (SR) to the previous studies

<table>
<thead>
<tr>
<th>High latitudes (&gt; 60°S)</th>
<th>Mid-latitudes (30°S – 60°S)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>65°S, 150 – 170°E</td>
<td>Super-100-142%</td>
<td>This study</td>
</tr>
<tr>
<td>Under: 85-100%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60°S – 66°S, 140°E</td>
<td></td>
<td>Yoshida et al., 2011</td>
</tr>
<tr>
<td>Jan: super- 100-210%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feb: under- 87-100%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60°N – 70°S, 140°W</td>
<td>97–109%</td>
<td>Bates et al., 1996</td>
</tr>
<tr>
<td>Under: 97-100%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>super: 100-102%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5°N – 42°S, 75-80°W</td>
<td>Super-110%</td>
<td>Kelly et al., 2002</td>
</tr>
<tr>
<td>Under- 90-100%</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.2 Monthly mean AOU, wind speed, the sea-air CH₄ flux in the Southern Ocean (south of 50°S)

<table>
<thead>
<tr>
<th></th>
<th>Dec</th>
<th>Jan</th>
<th>Feb</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean AOU (µmol kg⁻¹)</td>
<td>-2.5</td>
<td>-3.2</td>
<td>-0.1</td>
<td>-1.9</td>
</tr>
<tr>
<td>CH₄ saturation ratios (SR, %)</td>
<td>100.84</td>
<td>101.04</td>
<td>100.13</td>
<td>100.67</td>
</tr>
<tr>
<td>Mean wind speed (U, m s⁻¹) (avg 30 yrs)</td>
<td>6.9</td>
<td>6.78</td>
<td>7.44</td>
<td>7.03</td>
</tr>
<tr>
<td>CH₄ flux (µmol m² day⁻¹)</td>
<td>0.09</td>
<td>0.14</td>
<td>0.06</td>
<td>0.08</td>
</tr>
<tr>
<td>CH₄ emission (Tg yr⁻¹)</td>
<td>0.027</td>
<td>0.04</td>
<td>0.019</td>
<td>0.024</td>
</tr>
</tbody>
</table>
CHAPTER 4:
INFLUENCE OF A WARM-CORE EDDY ON
CH$_4$ DISTRIBUTION IN THE ARCTIC OCEAN

4.1 Dissolved CH$_4$ distribution in the Arctic Ocean

Large sources of CH$_4$ are stored in the Arctic (Shakhova et al., 2014). Large sources of CH$_4$ in the Arctic shelves contribute to the distribution of CH$_4$ in the water column (Damm et al., 2015b; Matveeva et al., 2015) and atmosphere (Myhre et al., 2016). In the Arctic Ocean, the principal sources of CH$_4$ are anaerobic methanogenesis in decaying organic matter in thawing permafrost, degradation of gas hydrates, and thermogenic CH$_4$ from cold seeps from hydrocarbon deposits (Reeburgh, 2007).

Release of unstable CH$_4$ hydrates is thought to be a large source of CH$_4$ emissions. This release occurs in shallow (Phrampus et al., 2014) and deep water (Coffin et al., 2013; Ruppel, 2015) in the Beaufort Sea, Eastern Siberian Arctic Shelf and Eurasian shelves (Shakhova et al., 2010a; 2014), which is generally considered the most sensitive to climate change effects (Kvenvolden, 1993; Ruppel, 2011). Previous studies show elevated CH$_4$ fluxes into seawater can potentially lead to increase CH$_4$ emission from the ocean into the atmosphere. In addition, extensive gas bubbling from the sea floor has been observed in the shallow water along the West Svalbard continental margin (Westbrook et al., 2009; Graves et al., 2015; Myher et al., 2016). Expelled CH$_4$ from sea floor is released into the water column and thus does not reach the atmosphere (James et al., 2016). Conversely, the recent publications have shown that high level of atmospheric CH$_4$ has considered as a release of oceanic CH$_4$ in the shallow areas (Myhre et al., 2016).

Some observations of CH$_4$ have been investigated in the Arctic Ocean (Shakhova et al., 2010; Damm et al., 2010, 2015; Lorenson et al., 2016; Fenwick et al., 2017; Li et al., 2017). Results of CH$_4$ observations have been reported as an evidence for high CH$_4$ emission in many areas of the Arctic shelves. High CH$_4$ in surface water (mean value of 18 nmol L$^{-1}$) has been attributed to the thawing of subsea permafrost on the Eurasian shelf (Shakhova et al., 2010a, Kosmach et al., 2015) while less CH$_4$ (average of 8.1 nmol L$^{-1}$) has been previously found in the permafrost-free Chukchi Sea (Kosmach et al., 2015). Significant CH$_4$ is also observed in the Beaufort Sea (up to 13.8 nmol L$^{-1}$) (Lorenson et al., 2016), however, amount of CH$_4$ is smaller than that of in the East Siberian Arctic shelves (ESAS) with large amount of CH$_4$.
escape from seabed into the water column (flux of ~70-450 nmol m$^{-2}$ s$^{-1}$ or 17 Tg yr$^{-1}$)) (Shakhova et al., 2014).

Amount of CH$_4$ stored within gas hydrates or from marine sediments releases into the water column and then reaches to the atmosphere is still unclear. Emitted CH$_4$ in the atmosphere could cause positive feedback and could accelerate climate warming (Ferré et al., 2012). Almost the previous studies have focused on biological processes that directly affect biological CH$_4$ production and consumption in the water column. Notwithstanding rare studies present combination of physical and biological factors affect the transportation of dissolved CH$_4$ or CH$_4$ distribution. In this research, I investigate the effects of eddies to CH$_4$ distribution in the water column.

4.2 Characteristics of water masses and eddies in the Arctic Ocean

Research area in Chapter 4 covers the Bering and Chukchi Seas and a part of Canada Basin. Thus, a brief introduction for its characteristics of water masses and eddies is described below.

4.2.1 Characteristics of water masses in the Arctic

Water masses in the Arctic Ocean have specific physical and biological features because of the interaction of freezing and melting processes in the water column, river run-off into the continental shelves and advection into the Arctic Ocean (Rudels et al., 1996). The Bering and Chukchi Seas are dominated by northward flowing Pacific water that comprises several distinct water masses such as Anadyr Water (AnW), Bering Sea Water (BSW), Pacific Winter Water (PWW), Pacific Summer Water (PSW) and Alaskan Coastal Water (ACW). The inflow water flows across the Chukchi Shelf including two or three distinct branches which governed by the bathymetry of the shoals and canyons (Paquette and Bourke, 1981; Weingartner et al., 1998; Woodgate et al., 2005). The western side of of the Bering Strait follows Herald Canyon (e.g., AnW) composing of lowest temperature, upwelled, saline, nutrient-rich deep water. A central inflow follows the Central Channel with intermediate salinity is unknown as BSW. In the eastern side, the inflow is dominated in late-spring to early-fall by the warm, relatively fresh ($S < 31.8$), nutrient-poor ($<1.5$ µmol L$^{-1}$ NO$_5$) ACW (Paquette and Bourke, 1974) as a part of the PSW (Shimada et al., 2001). Pacific water flows into Arctic Ocean with composing of PWW and PSW but the difference between PWW and PSW results from the period of seasonal sea-ice growth. In the winter, convective overturning caused by brine rejection during sea-ice formation, this process helps to stir up the sediments and add regenerated sedimentary nutrients.
to PWW (Pickart et al., 2016). PSW (S = 31-32, T>-1°C, D = 25-26σt) is found between 40-100m while PWW (S = 32-33.1, T<-1°C, D = 26-26.5σt) lies between ~100-200 m or deeper water characterizing by low temperature and high salinity feature (Woodgate et al., 2005).

When Pacific water transit over the shallow Bering and Chukchi shelves into the Arctic Basin and are modified by biological and physical processes (Yamamoto-Kawai et al., 2006) from both of the surface water and above sediment layer (Cooper et al., 1997). During summer the fresher, warmer and northward flowing PSW gradually displaces the PWW even though the appearance of remanent PWW exists on the northern Chukchi shelf (Pickart et al., 2016).

The Canada Basin comprises deep water (~4000 m), which is bordered by shallow seas and continental shelf. Surface water of the Canada Basin is characterized by a Polar Mixed Layer (PML) of about 40 m depth, which is relatively fresh (S ~ 26-31.2) and is nutrient-depleted (Macdonald et al., 2004; Carmack et al., 2006). Dense PWW sinks to the deepest area of the canyon (below 35 m depth) and is overlain by PSW and ACW (5-35 m) as well as a surface melt-water layer (0-5m) (Gong and Pickart, 2015). When Pacific water enters the Canada Basin from the Chukchi Sea, it subducts below the PML into the Upper Halocline Layer (UHL). Below the UHL, the halocline layer occupies a depth range of ~200-400 m and derives from Atlantic origin water while Canada Basin Intermediate Water (CBIW) occupies at a depth range of 400-2000 m. Canada Basin Deep Water (CBDW) is found below 1500 m depth, which is relatively homogeneous and has been isolated from the atmosphere for about 450 years (Timmermans et al., 2003).

4.2.2 Introduction to eddy in the Arctic Ocean

Chukchi Sea, Beaufort Sea and Canada Basin are populated with a large number of sub-mesoscale eddies (Muenchow et al., 2000). Three types of eddies have been observed in the southern Canada Basin. Firstly, warm-core surface-intensified eddies (0-50 m) contains Alaskan Coastal water, which belongs to the season (late-summer/early-fall). Other two types of eddies which occur in subsurface water, are either a cold- or a warm-core. The former is spawned during spring and early summer when the current is advected dense and cold water. The latter are formed later in fall when the boundary current has been replaced with PSW, which is warmer in summertime Chukchi Sea shelf water.

The primary difference between both eddies is characteristics of itself water-core including physical, chemical and biological parameters. The most commonly observed type of eddy in the southern Canada Basin is the sub-surface cold-core anticyclone (S = 33.1; T = -1.6°C) (Pickart and Stossmerster, 2008) with a diameter of 10-20 km (Manley and Hunkins,
1985) and thickness of 75 m (Mathis et al., 2007). In contrast, warm-core eddies are rarely detected by oceanographers with a small fraction of the total eddies (3%). This water-core entirely is warmer than ambient environment, coming subsurface water of PSW. The warm-core eddies also transport heat and nutrients from the Chukchi Sea shelf to the Canada Basin like cold-core eddies (Mathis et al., 2007; Nishino et al., 2011; Kawaguchi et al., 2012; Watanabe et al., 2014) but the warm-core water may control nutrient distribution and affect primary production in the euphotic zone (Nishino et al., 2011). Enhancement of the magnitude of the biological pump attributed to arising of eddies, driven transport of shelf-origin nutrients and biological materials towards the Canada Basin (Watanabe et al., 2014). Even though the frequency of the occurrence of warm-core eddies is rare (accounting for 3% of the total number), its role in transporting material is undeniable. Few studies of warm-core eddies has examined their influences on the nutrient distribution and biological activities but the effect on CH$_4$ distribution that has not been investigated yet until now. Therefore, this study focuses on the impact of warm-core eddies on CH$_4$ distribution in the Arctic Ocean.

4.3 Data and Methods

4.3.1 Field sampling

Over the period from August to October 2015, seawater samples were collected on R/V Mirai (MR15-03 Leg.1, Fig. 4.1a) from surface water to the bottom water. A warm-core eddy was observed in the shelf-slope of the Chukchi Sea during the cruise. Majority of sampling was conducted over Chukchi Sea shelf-slope and the southwestern Canada Basin (see Fig. 4.1b), to identify the vertical distribution of CH$_4$ concentration inside/outside of the eddy zone. Vertical seawater samples were taken using 12-L Niskin bottles mounted on a CTD rosette for analyses of dissolved CH$_4$. Approximately 170 seawater samples were collected at 19 stations for the CH$_4$ analysis. A Sea-Bird CTD system (SBE9plus, Sea-Bird Electronics Inc., WA, USA) equipped with ancillary sensors was used to measure salinity, temperature, and other hydrographic parameters. These CH$_4$ samples were measured at Nagoya University by GC, and description of GC system is also mentioned in Chapter 2. The cruise crossed some distinct water masses such as PSW, PWW, ACW, MW, and Atlantic Water (AW); and crossed the warm-core water.

Another measurement system is CRDS system coupling with an equilibrator which is described in detail in Chapter 2. It was deployed to obtain mixing ratios of CH$_4$ at that time during the cruise.
The atmospheric concentration of CH$_4$ was taken as 1850 ppb, based on the average mixing ratios in Barrow, Alaska in 2015 (Data provided by NOAA ESRL Global Monitoring Division, Boulder, Colorado, USA).

4.3.3 Chemical and Biological Oceanography parameters

4.3.2.1 Dissolved Oxygen (DO)

Seawater samples were collected with Niskin bottle attached to the CTD-system and transferred from bottles to a calibrated flask of 100 cm$^3$ with overflowing of 3 times volume of the flask. Then two reagent solutions (Reagent I and II) of 0.5 cm$^3$ were added immediately into the sample flask and the stopper was sealed carefully. The sample flask was shaken at least twice to mix the content and dissipate the precipitate. At least 2 hours after shaking, 1 cm$^3$ sulfuric acid solution and a magnetic stirrer bar were added to the sample flask and stirred. These samples were measured by using a burette for sodium thiosulfate and potassium iodate APB-510/APB-620 (Kyoto Electronic Co. Ltd, Japan)

AOU is the difference between the measured dissolved oxygen concentration and its equilibrium saturation concentration in water. It is defined in section 2.6 Chapter 2.

4.3.2.2 Nutrients

Nutrients data included ammonium (NH$_4^+$), nitrate (NO$_3^-$), nitrite (NO$_2^-$), phosphate (PO$_4^{3-}$) and silicate (SiO$_2^-$) were analyzed by using a QuAAtro 2-HR system. Fixed nitrogen (N**) values were calculated as a measure of the relative excess or deficit of fixed nitrogen relative to phosphate (see section 2.6 Chapter 2; Codispoti et al., 2005a). These biological parameters (e.g., nutrients) allow us to constrain the biogeochemical processes that influence on trace gas cycling.

4.4 Existence of a warm-core eddy during the cruise

During the cruise, a warm-core eddy was observed in the Chukchi Sea shelf slope and near Barrow Canyon. The position of the warm-core eddy is pointed out in Fig. 4.2. In general, the warm-core eddy appeared near the surface or at a depth range was shallower than the depth of cold-core eddy (Pickart and Stossmerster, 2008). This eddy appeared near the surface at depths of 20–70 m (Fig. 4.2b), and the core of the eddy was characterized by potential temperatures of 4–6°C at a depth of 50 m. The characteristics of the water mass indicated that the warm water had been derived from Pacific Summer Water (PSW) (salinity = 31–32;
temperature > –1°C) (D’Asaro, 1988). This warm-water core was distributed laterally along an isopycnal plane with a potential density ($\sigma_\theta$) of ~24–25. The patch of warm water created a sharp thermohaline front against the surrounding water to the north (72°N or at 100 and 150 km) that resulted in a horizontal velocity maximum shear with a squared magnitude of $(1–2) \times 10^{-4} \text{s}^{-2}$ (Kawaguchi et al., in preparation). The interior of the warm core was characterized by a low Brunt-Vaisala frequency (N) of about 3 cycles per hour (Fig. 4.2b) Kawaguchi et al. (in preparation) have pointed out that the magnitude of the maximum tangential velocity within the warm-core radius was about 0.55 cm s$^{-1}$. The colder and denser water below the warm water, which was characterized by a salinity (S) of 32–33 and $\sigma_\theta$ of 25–26, was determined to be Pacific Winter Water (PWW). The location of the warm water mass in a subsurface layer suggested that it was a warm-core eddy. The eddy was presumed to have formed over the Chukchi Sea shelf and to have been advected laterally into the cold water above the shelf slope. The eddy was a thin, about 30–50 m thick, and its diameter was 30–50 km. Eddies can transport warm water (PSW, ACW) to a depth of 70 m or more but still lie above the upper boundary of PWW.
4.5 Results and discussion

4.5.1 Spatial distribution of dissolved CH₄ distribution in high latitudes

4.5.1.1 Spatial distribution of dissolved CH₄ from CRDS measurement

Continuous dissolved CH₄ concentration range was 2.6-17.6 nmol kg⁻¹ in the surface seawater with an averaged value of 4.6 nmol kg⁻¹ (Fig. 4.3) over the whole region. Dissolved CH₄ concentration in the surface was supersaturated (103-514%), averaging 137.9% in the surface water. CH₄ concentration increased considerably from south Bering Strait (ca. 3 nmol kg⁻¹) to the northern Chukchi Sea (17.6 nmol kg⁻¹). High CH₄ concentration was double near the Point Hope with a value of 7.7 nmol kg⁻¹ in the Bering Sea (SR = 235%; F₇CH₄ = 2.25 µmol m⁻² d⁻¹). In addition, high CH₄ concentration the Chukchi sea shelf slope (72°N) was 17.6 nmol kg⁻¹, which was also observed by Li et al. (2017). The CH₄ maxima at the shelf break (72°N) may be resulted of diffusion from bottom water into the water column (Li et al., 2017).

4.5.1.2 Spatial distribution of dissolved CH₄ from GC measurement

Over whole region, dissolved CH₄ concentration range was 4.8-14.3 nmol kg⁻¹ and the average was 6.4 nmol kg⁻¹ in near-surface seawater (10 m depth) (Fig.4.3a). Dissolved CH₄ was obviously supersaturated (range: 141-416%; average 185%) in the surface seawater. In comparison, the CH₄ concentration in near surface seawater in this study was generally lower
than that reported in the previous reviews (10.08 nmol kg\(^{-1}\), Li et al., 2017; 11.2 nmol kg\(^{-1}\), Savvichev et al., 2007).

Near the coast, CH\(_4\) concentration was as high as up to 14.3 nmol kg\(^{-1}\) (SR = 416%), it was 2.5 times higher than surrounding surface water (~5 nmol kg\(^{-1}\); SR ~150%). At the stations with shallow water depth (~50 m), dissolved CH\(_4\) concentration increased with depth to the bottom (Fig. 4.4 b,c). At a few stations with a water depth of ~200 m (Fig. 4.5), the CH\(_4\) concentration increased with depth up to 50 m but decreased with depth at greater depths. The lowest CH\(_4\) concentration at 200 m depth was 1.7 nmol kg\(^{-1}\) (SR = 48.8%) in the deeper water. In this study, the observed CH\(_4\) concentration was lower in Atlantic-derived water than in Pacific-derived water (PSW, PWW and ACW) (Fig. 4.6). The highest CH\(_4\) supersaturation appeared in bottom water above the sediment. In that water the SR of 947% (35.81 nmol kg\(^{-1}\)) probably resulted from high in situ methanogenesis of organic matter in the sediments (Reeburgh, 2007) and diffusion of the produced CH\(_4\) into the water column. High CH\(_4\) production at the Chukchi Sea shelf may be laterally transported into the Canada Basin by ACW (Matveeva et al., 2015). The ACW captured higher CH\(_4\) from riverine before it came to Chukchi Sea, which result from the methanogenesis of organic matters in degradation of permafrost (Striegl et al., 2012). In contrast, Ruppel (2015) reported that there is no influence of subsea permafrost or gas hydrate on the elevated CH\(_4\) in water column, but it may results from methanogenesis in the sediments. In general, the degree of CH\(_4\) supersaturation in the Chukchi Sea was smaller than that of the East Siberian Sea (ESS), had been reported by Shakhova et al. (2010).

The Chukchi sea is a productive regions because of its high primary productivity, large quantity of particulate organic matter settles to the sea floor (Grebmeier et al., 2006; 2015; Lepore et al., 2007). It may support for high rates of microbial processes for CH\(_4\) formation in the upper sediments (Savvichev et a., 2007). At the shelf break, CH\(_4\) concentration exceeded the equilibrium concentration with the atmosphere by 3 orders of magnitude. Maxima CH\(_4\) concentrations at the bottom would have been released upward and diluted. A few CH\(_4\) hotspot within the Chukchi Sea has been revealed (Savvichev et al., 2007).

4.5.2 Sea-air CH\(_4\) flux

There was a minor source of CH\(_4\) with sea-air flux averaging 1.02 µmol m\(^{-2}\) d\(^{-1}\) (ranged from 0.001 to 19.45 µmol m\(^{-2}\) d\(^{-1}\)) from CRDS system was compared to 2.4 µmol m\(^{-2}\) d\(^{-1}\) (Fig. 4.7) measuring from GC.
Sea-air fluxes of CH$_4$ in this study from southwestern Canada Basin were approximated the observed CH$_4$ emission of Fenwick et al. (2017) in the Bering Sea (0.2 µmol m$^{-2}$ d$^{-1}$), in the Canada Basin (1.3 µmol m$^{-2}$ d$^{-1}$) and in the Chukchi Sea (1.9 µmol m$^{-2}$ d$^{-1}$).

4.5.3 Comparison of dissolved CH$_4$ distribution inside and outside of the warm-core eddy

Comparison of vertical profiles of dissolved CH$_4$ concentration within and outside the warm-core eddy is shown in Fig. 4.8. CH$_4$ concentration peaked at approximately 50 m and 100 m depth outside and inside the eddy, respectively. I hypothesize that the greater thickness of subsurface CH$_4$ peaks inside than that outside the warm-core reflected the characteristics of the eddy. Which factors may have been responsible for this phenomenon?

Does in situ CH$_4$ production in the water column affect the subsurface CH$_4$ peaks? We could not detect spreading of dissolved CH$_4$ from either the sea surface or from the bottom water (Fig. 4.8). Is there a contribution from in situ production in the water column? If a large amount of CH$_4$ production occurred in the water column, a large source of particulate organic matter would be needed. However, there was no clear correlation between chlorophyll-$a$ concentration and CH$_4$ at the subsurface water (0-50 m depth). In addition, CH$_4$ concentrations were correlated with the concentrations of nutrients such as ammonium, phosphate, and silicate (Fig. 4.10). The similarity of the characteristics of the subsurface nutrient peaks and the dissolved CH$_4$ concentrations implies that there was in situ source of CH$_4$ in the subsurface water. The CH$_4$ maxima at 100-200m depth might be transported laterally along the broaden shelf water or by Alaskan Coastal Current (Hioki et al., 2014; Kudo et al., 2018). Besides, another mechanism, such as ocean physics, needs to be considered.

Do physical factors (e.g., seawater temperature) affect the distribution of CH$_4$? At the shelf stations, CH$_4$ supersaturation was detected where the seawater temperature was high (up to 6$^\circ$C) and the salinity low. Inside the warm core, the water temperature was as warm as 5–6$^\circ$C, whereas below the warm core the water was relatively cold (~1.46$^\circ$C) and dense. Salinities inside and outside the warm core were the same (30.9), but the temperatures differed, 4.39$^\circ$C and 1.18$^\circ$C, respectively. The corresponding methane solubilities were 3.25 and 3.55 nmol kg$^{-1}$, respectively. The difference in CH$_4$ solubilities was 2.9%, whereas the difference in CH$_4$ saturation was 13.5%. Physical processes such as seawater temperature therefore did not strongly affect the spreading of subsurface CH$_4$ concentration.

The spreading of CH$_4$ that occurs in a warm-core eddy may explain the entrainment and lateral transport of warm-core water from the shelf water. A maximum tangential velocity of
about 0.55 cm s\(^{-1}\) in magnitude was observed within the warm core, as we mentioned above. In addition, remarkable maxima of vertical shear were found along the top and bottom of isopycnals corresponding to \(\sigma_g = 24.5\)–25.0 and 26.0–27.0 kg m\(^{-3}\) (corresponding to depths of 50, 100, and 150 m, respectively). A broad extension of sub-surface CH\(_4\) peaks was therefore present inside the radius of the eddy where the shear velocity was a maximum. The spreading that occurred inside of warm-core eddy can therefore be explained by entrainment of CH\(_4\) from shelf water associated with nutrients’s tracer.

4.5.4 Eddies transport CH\(_4\) from shelf-slope into the basin

The primary mechanism of water that is transported off shelf water into the interior basin in the Arctic by ocean currents remains largely unclear. One possible mechanism is formation of eddies at or near the continental shelf-break in the Chukchi/Beaufort Seas, migrates the water into the central basin including nutrients (Nishino et al., 2011), implying the eddy can transport dissolved CH\(_4\) at the same time. I would like to discuss whether the eddy has the meaningful role in transporting of CH\(_4\) into the southwestern Canada Basin.

By tracking sub-sections, I could see that warm-core eddies apparently helped to transport dissolved CH\(_4\) from the shelf slope (35.81 nmol kg\(^{-1}\) at sta.47) into the basin and transported the CH\(_4\) into deeper water (32.3 and 18.7 nmol kg\(^{-1}\) at sta. 37 and 35, respectively) (see Fig. 4.9). Possible mechanism contributing to CH\(_4\) transport in this area was lateral transport, which would have carried dissolved CH\(_4\) from the shelf-slope into the Barrow Canyon and Canada Basin. A CH\(_4\) “hotspot” at a distance of 150 km from the coast appeared at the deeper water. This hotspot may have resulted from downward transport in the warm-core eddy further northward.

In this study, I detected the influence of warm-core eddies on the transport and distribution of dissolved CH\(_4\) in the water column even though it accounted for only about 3% of the total number of eddies in the western Canada Basin and Chukchi Plateau (Plueddemann and Krishfield, 2007). However, approximately 125 cold-core eddies per year that occur in Arctic water may affect material transports at the shelf water if these eddies have an average radius of 10 km and a thickness of 75 m (volume of 25 km\(^3\)) (Pickart et al., 2005). Cold-core (anticyclonic) and warm-core (cyclonic) eddies probably transport dissolved CH\(_4\) in similar ways.

A basic difference, however, between anticyclonic and cyclonic eddies is the mechanism that pulls down or lifts up subsurface CH\(_4\) peaks, respectively. This difference between the eddies would affect the timing of CH\(_4\) release and removal mechanism from the
shelf. A cyclonic warm-core eddy may lift up sub-surface CH₄ peaks until the eddy dissipates. The CH₄ is diluted and eventually released into the atmosphere because the CH₄ is volatile. A warm-core eddy contributes directly to advection of CH₄ at the shelf break and in the upper halocline. This eddy transport was directly responsible for maintaining CH₄ maxima at 100 m depth at eddy stations in the southwestern Canada Basin in our study. In a cold-core eddy, this process may affect the release of CH₄ into the atmosphere from the shelf water. Mathis et al. (2007) estimated the amount of nutrients that eddies remove from the shelf and concluded that cold-core eddies are the dominant removal mechanism in the western Arctic Ocean. Even though we assume that cold-core eddies contribute to CH₄ effluxes compared to warm-core eddies, we have not yet observed CH₄ transport in a cold-core eddy. Future field observations including of cold-core eddies will be needed to obtain a comprehensive understanding of how eddies affect CH₄ distributions.

4.5.5 Correlation between CH₄ and Nutrients

High concentrations of nutrients (e.g., ammonium, phosphate, silicate) are characterized for large amount of organic matters link to CH₄ methanogenesis. High ammonium concentration during summer indicates for decomposing of organic matter which is deposited on the Chukchi Sea shelf (Cooper et al., 1997; Nishino et al., 2005). Ammonium concentration increased rapidly up to 3.4 µmol kg⁻¹ at a depth of 40-50 m compared to the continental shelf. A ammonium plume at a distance of 150 km from the coast was found at 70-150 m depth with concentration of 2.6 µmol kg⁻¹ (Fig. 4.10a), which was at the same depth to the CH₄ hotspot. Nevertheless, at the northern of the continental shelf slope, ammonium concentration was low and almost close to zero. Plumes of silicate and phosphate were also observed at the same depth of ammonium (Fig. 4.10b, c). In contrast, nitrate concentration was increased rapidly at a depth of 70-80 m at the center of the transect (Fig. 4.10d). At 150-km distance from the coast, the warm-core eddy contained high ammonium, high-silicate and high-phosphate contents compared to the surrounding water. It is completely different from Nishino et al. (2011) reported that the warm-core eddy packed the low-silicate and low-phosphate water. The warm-core eddy could carry high concentration nutrients trapped on the shelf water during formation to Canada Basin.

Negative values of fixed nitrogen (N**) indicate the occurrence of significant denitrification within the shelf sediments (Codispoti et al., 2005a; Gruber and Sarmiento, 2009). Minimum values of N** was observed at the shelf water, and lied on isoline of 32-33 or 25-26σθ. In particular, minima N** (-12.3 µmol kg⁻¹) correlated to maxima nutrients (NO₃⁻: 14.71
µmol kg⁻¹, \( \text{PO}_4^{3-} \): 1.765 µmol kg⁻¹) (Fig. 4.10) at the same layer in the UHL (< 200 m) because \( N^{**} \) derived from the nitrogen and phosphate concentration. Low nitrate concentration is probably attributable to low \( N^{**} \) values in the Bering shelf water. The similarity of minimum \( N^{**} \) has been reported at the same depth by Hioki et al. (2014). During denitrification process, nitrate is consumed instead of oxygen during the bacterial decomposition of organic matter in low-oxygen water in the sediment pores. This process causes a reduction in \( N^{**} \) which is found in the Bering/Chukchi Seas (Devol et al.; 1997; Yoshikawa et al., 2006) and indicates a net loss of nitrate in the ocean interior (Devol et al., 1997).

Strong correlations at the coast were found between \( \text{CH}_4 \) and \( \text{NH}_4^+ \) (\( \text{CH}_4 = 9.11 \times \text{NH}_4^+ + 4.52, R^2 = 0.87, n = 20 \)); silicate (\( \text{CH}_4 = 0.62 \times \text{SiO}_2^{2-} + 3.35, R^2 = 0.77, n = 20 \)); and phosphate (\( \text{CH}_4 = 25.07 \times \text{PO}_4^{3-} - 9.28, R^2 = 0.77, n = 20 \)); fixed nitrogen (\( N^{**} \)) was: (\( \text{CH}_4 = -5.49 \times N^{**} - 28.37, R^2 = 0.8, n = 20 \)). This finding implies that \( \text{CH}_4 \) is produced at the shelf stations where response for high primary productivity and large quantity of particulate organic matters settling to the seafloor (Grebmeier et al., 2006, 2015; Lepore et al., 2007) with a high rate of microbial \( \text{CH}_4 \) processes in the upper sediments (Savvichev et al., 2007). This result is consistent with previous research that obtained high \( \text{CH}_4 \) concentration upper the sedimentary in the Chukchi Sea shelf (Matveeva et al., 2015; Li et al., 2017).

Apparent oxygen utilization (AOU) was high (> 60 µmol kg⁻¹) (Fig. 4.10) near the bottom layer at the coastal stations indicated low dissolved oxygen (DO) concentration even though it still maintained aerobic biological activities. Above the sedimentary layer, \( \text{CH}_4 \) concentrations was high as well as AOU concentration. A positive correlation between AOU and \( \text{CH}_4 \) at coastal station 47 (\( \text{CH}_4 = 0.276 \times \text{AOU} + 17.64, \text{or} \ SR = 6.90 \times \text{AOU} + 489.56, R^2 = 0.6 \)) means \( \text{CH}_4 \)-rich water or existence of \( \text{CH}_4 \) production at the positive AOU. At the other stations without effect of the eddy, a negative correlation between AOU and \( \text{CH}_4 \) (\( \text{CH}_4 = -0.05 \times \text{AOU} + 7.18 \text{ or} \ SR = -1.617 \times \text{AOU} + 206.42, R^2 = 0.62 \)) was found.

In this study, a distinct \( \text{CH}_4 \) maxima occurred at which corresponds to the near isoline of 32 that is similar to the publication of Li et al. (2017). Profiles of nutrients, \( N^{**} \) and \( \text{CH}_4 \) against to potential density (\( \sigma_\theta \)) showed a well-developed halocline in the range of 24-27.5 \( \sigma_\theta \) (Fig.4.11). In the shelf water, maximum \( \text{CH}_4 \) was observed in the bottom water (\( \sigma_\theta \approx 26 \)). The fact that the maximum concentration of nutrients and \( N^{**} \) occurred at \( \sigma_\theta \approx 26 \) in the shelf, slope and further region; it strongly suggests the lateral transport of these nutrients and \( \text{CH}_4 \) from cold and dense bottom water (\( T \leq 1^oC, S \sim 32, \sigma_\theta \approx 26 \)) of the shelf to the halocline in the shelf slope region. Amount of organic matters is delivering to in the upper halocline water, it would be contributed to oxygen consumption in shelf slope of the Canada Basin. We suggest
that the subsurface CH$_4$ maxima originates from the shelf water as a result of northward spreading water by oceanic currents and propagation of the eddy.

4.5.6 Correlations between nutrients and CH$_4$ inside/outside the warm-core eddy

The relations of CH$_4$ and nutrients at the coastal station have been found in the previous section. These nutrients and CH$_4$ could be simultaneously trapped and maintained within the warm-core during transporting from shelf water to the southwestern Canada Basin. As if the relations between them are the same within and outside the eddy, the relations between CH$_4$ and nutrients between within and outside of the eddy are considered as follows.

For ammonium at outside the eddy, the correlation between them was agreed well (CH$_4$$_{outside}=9.6\times$NH$_4$ +5.3, $R^2=0.81$) (Fig. 4.12). Within the eddy, it showed weaker correlation (CH$_4$$_{inside}=7.97\times$NH$_4$ + 5.15, $R^2=0.64$) comparing to the outside. Lower concentration of CH$_4$ inside the eddy is discussed in the previous section. Lesser concentration ammonium inside the eddy may be caused by physical factors (e.g., later transport, mixing or dilution) or by biological factors (ammonium is taken up by phytoplankton’s existence) (Nishino et al., 2011).

For nitrate, phosphate, and N$^{**}$: Fig. 4.12 showed lesser correlation within the eddy than at the outside eddy. Because they are non-conservative and are easily consumed by nitrification and denitrification (Codispoti et al., 2001; Nishino et al., 2005). However, both of them have the same distributional structure between within and outside the eddy with CH$_4$. I suggest the relation of CH$_4$ and each nutrient is a similar feature between within and outside the warm-core eddy.

Phytoplankton may be affected by the warm-core eddy. The chl-$a$ concentration was high on the shelf area (sta. 47 and sta.15) and the shelf slope, for example, at the sta. 23 and sta. 30 (Fig. 4.13). However, integrated chl-$a$ concentration over the warm-core eddy (sta. 37) was lower than that of the water outside the eddy in the top of 50 m layer (approximately the euphotic zone) is shown in the Fig. 4.13. The chl-$a$ concentration of large phytoplankton (> 10 µm) drastically decreased between the shelf area comparing to the eddy area (green bars). Chl-$a$ concentration of 2-10 µm was slightly higher in the shelf area than within the eddy and shelf-slope (red bars). There is no different from chl-$a$ concentration of picoplankton (< 2 µm) (blue bars) between stations. In the shelf area, large phytoplankton is dominated such as diatoms because of high concentration of nutrients in the euphotic zone. Diatoms can uptake and store nutrients at a more rapid rate than picoplankton can (Smetacek, 1998). Over the warm-core eddy (sta. 37), composition of size-fractionated chl-$a$ was similar to at the shelf water (sta. 47
and sta. 15), but chl-α concentration itself was low. It might be caused by the maintenance of large phytoplankton inside of the eddy.

### 4.5.7 Correlation between CH₄ saturation (SR) and AOU at isoline of 32 and N⁎⁎ minimum layer

Lateral transport supplied negative N⁎⁎, CH₄ and nutrients from the shelf water into the basin interior as well as AOU. Maxima CH₄ linked to negative N⁎⁎ values and positive AOU at the coastal station. Observed CH₄ maxima was discovered on the isoline of 32 (Li et al., 2017) in the Chukchi shelf and was also detected on the isopycnal of ~26σθ in the UHL (Fig. 4.10e) (Hioki et al., 2014). AOU indicates for oxygen utilization of organisms, CH₄ production could be detected with high AOU concentration. Thus, correlation between CH₄ (or SR) and AOU is expected to find (Fig. 4.14). In general, SR and AOU have a negative relation excepting for some scattered points in two ellipsoids (Fig. 4.14). The relation shows high CH₄ agreed to low AOU concentration in the aerobic water, which could be derived from rich-CH₄ water from the bottom water by mixing processes. A negative correlation outside the warm core indicates that CH₄ is generally oxidised in the aerobic environment (Fig.4.15a) except for coastal stations.

On the contrary, inversed relation between SR and AOU appears for coastal station and inside the warm-core water, are shown as scattered points in the upper trend arrow. The positive correlation points out that it is completely different from general case (Fig. 4.14) showing in two ellipsoid shapes. CH₄ production requires strictly anaerobic conditions by microbes in hypoxic microenvironments (sinking organic particles and within guts of zooplankton). However, high CH₄ is consistent with positive AOU even though low dissolved oxygen indicates for the aerobic environment reflected CH₄ supply from low dissolved oxygen upper sedimentary. For scattered blue circles, it is obtained from the shelf water which is discussed in the previous section. For scattered yellow circles is shown in Fig. 4.14 the positive correlation derives from the warm-water core (Fig. 4.15b, SR = -4.172×AOU + 503.92; R² = 0.87). Two correlations between SR and AOU has a similar pattern to at the shelf water but lower CH₄ concentration was observed. Within the warm-core, water-core is isolatable to contact with surrounding water to exchange oxygen-rich water. Low dissolved oxygen within the warm-core was caused by oxygen consumption to maintain biological production via remineralization (Mathis et al., 2007) and/or biological activities.

The high CH₄ concentrations observed inside the warm-core radius were trapped as the vortex formed and propagated. As the eddy spread, local in situ CH₄ production and oxidation may have occurred. CH₄ can be produced in small anaerobic environments in organic particles
Methane oxidation rates of 0.0038 nmol hr\(^{-1}\) (= 0.0912 nmol day\(^{-1}\)) and 0.03–0.09 nmol day\(^{-1}\) have been reported in the Beaufort Sea (Kitidis et al., 2010) and above the Chukchi Sea shelf (Savvichev et al., 2007), respectively. Here I assumed that CH\(_4\) oxidation occurred during the week when the eddy was propagating. The average calculated CH\(_4\) concentration inside the warm core after 7 days was calculated to be 18.91 nmol kg\(^{-1}\) and 23.52 nmol kg\(^{-1}\), respectively, with initial CH\(_4\) concentration of 35.81 nmol kg\(^{-1}\). However, the observed CH\(_4\) concentration inside the warm core was 32.3 nmol kg\(^{-1}\), higher than the calculated CH\(_4\) concentration (Table 4.3). Matveeva et al. (2015) have indicated that the loss of CH\(_4\) from the Chukchi Sea shelf are caused by ocean currents, mixing, and diffusion. Thus, within the warm-core eddy, CH\(_4\) was produced, or methane oxidation rates were lower than 0.06 nmol day\(^{-1}\). I therefore speculate that both CH\(_4\) losses caused by currents, mixing, and diffusion and CH\(_4\) production contributed to the CH\(_4\) distribution inside the warm core during propagating of the eddy.

### 4.5.8 Nitrous oxide (N\(_2\)O)

Nitrous oxide concentration in the southwestern Canada Basin ranged from 9.0 to 24.4 nmol kg\(^{-1}\) (saturation range: 71.5-161.6%), with a difference in a distinct water masses. In the surface freshwater layer, low concentration of N\(_2\)O was observed in river-input or melt-water (MW) and in the ACW whereas higher N\(_2\)O extent in the PSW (Fig. 4.17). The N\(_2\)O concentration was almost supersaturated respecting to atmospheric N\(_2\)O, with maximum concentration up to 16.7 nmol kg\(^{-1}\) (SR = 111%). In contrast, high concentrations of N\(_2\)O were observed in the PWW due to mixing in the shallow water in early spring and summer. In shallow Pacific water masses (PSW, ACW, MW) (< 25.5\(\sigma_t\)) in the southwestern Canada Basin, N\(_2\)O concentrations that were low close to atmospheric N\(_2\)O equilibrium. It implies that processes in this region likely a combination of sea-air exchange and dilution with low N\(_2\)O water masses, it leads to decrease in N\(_2\)O concentrations. N\(_2\)O maxima was also observed on the 26\(\sigma_t\) isopycnal line (S≈32) like CH\(_4\) that is transported from the shelf water off-shore into the basin interior, was discussed in the previous section of CH\(_4\) distribution. In deeper water, N\(_2\)O concentrations tend to decrease with increasing density, low N\(_2\)O concentration was observed with a mean value of ~15 nmol kg\(^{-1}\) and 97% saturation. This observation is relatively consistent with the recent observation of Zhang et al. (2015) and Fenwick et al. (2017).

A negative correlation between ΔN\(_2\)O and \(N^{**}\) is examined that providing an important evidence of N\(_2\)O source. The correlation implies the denitrification is a primary source of N\(_2\)O from sediment into the water column like Zhang et al. (2015) and Fenwick et al. (2017) strongly
suggested that the N\textsubscript{2}O production from the sediment of the Bering Sea and Chukchi Sea are a primary source in the Arctic Ocean. However, no relation between N* and N\textsubscript{2}O has been found because of its significant scatter (R\textsuperscript{2} = 0.067). This could be attributed by another process impacting on the N\textsubscript{2}O production. Recently, processes of denitrification-nitrification coupling have played a significant process in the nitrogen cycle on the sediments of the Bering and Chukchi shelves (Horak et al., 2013; Brown et al., 2015) and N\textsubscript{2}O production (Naqvi et al., 1998). However, the trend of N* and \Delta N\textsubscript{2}O shows that denitrification may work as a N\textsubscript{2}O source in this region.

4.5.9 DMSP as a precursor of methane

CH\textsubscript{4} could be produced from methylated compounds primarily and from a metabolic by-product of algae, which are considered to be a source for methanogenesis (Scranton and Brewer, 1977; Scranton et al., 1995). One of the methylated compounds produced by marine phytoplankton is DMSP (Keller et al., 1989). Primary production or phytoplankton abundance in the Arctic Ocean is regulated by nutrients in seawater while DMSP accounts only for less than 10% of total phytoplankton carbon (Kiene et al., 2000). In this study, DMSP\textsubscript{t} correlated with chl-\textalpha concentration with DMSP\textsubscript{t} = 0.25\timeschl\textalpha + 0.63 (R\textsuperscript{2} = 0.64, n = 22). In situ excess CH\textsubscript{4} is produced during phytoplankton bloom, and DMSP and its degradation product in oxygen-rich polar water (Damm et al., 2008; 2010) has been reported, but no correlation between them did obtain in this study. CH\textsubscript{4} is not agree well to DMSP\textsubscript{t} because of the effect of high production of CH\textsubscript{4} from marine sediment release.

4.6 Summary and Conclusion

During the cruise of the R/V Mirai (MR15-03 Leg.1) in summer 2015, CH\textsubscript{4} observation was examined to investigate vertical profiles of CH\textsubscript{4} in the Bering Sea to the Chukchi Sea and southwestern Canada Basin. Seawater samples were collected within and outside the warm-core eddy. A CRDS coupled with a shower head type equilibrator was also used to obtain continuous underway measurements of the mixing ratios of CH\textsubscript{4} in the surface water. In the surface seawater, CH\textsubscript{4} was slightly supersaturated overall region from 103-514% from CRDS system measurement. In additional, both undersaturated and supersaturated CH\textsubscript{4} ranged 49-947% in the southwestern Canada Basin from surface seawater to the bottom with extremely high CH\textsubscript{4} concentration (947% SR) reflected decomposing of organic matters.

The warm-core eddy was observed in the southwestern Canada Basin. The vertical profiles of CH\textsubscript{4} were examined within and outside the eddy. I found high CH\textsubscript{4} concentrations
in bottom water on the shelf, which located outside the warm-core eddy. I also found that sub-
surface CH$_4$ peaks within the radius of the maximum velocity of the eddy were broader at depth
than that outside the eddy. Lateral transports of ocean currents and propagating of the eddy
were likely the controlling factors responsible for subsurface peaks within the warm-core water.
This mechanism could carry high CH$_4$ at the shelf water and transport to the shelf-slope water
and Canada basin interior. Furthermore, nutrients (e.g., ammonium, phosphate, and silicate,
fixed nitrogen) were also conveyed as well as CH$_4$. Two patterns of the correlation between
SR and AOU were found. Negative correlation obtaining outside the warm core indicates that
CH$_4$ is generally oxidised in the aerobic environment. In contrast, positive correlation at the
coastal stations indicates high CH$_4$ in the aerobic water which could be derived from rich-CH$_4$
water or CH$_4$ diluted upward from upper sedimentary release with positive AOU into the water
column. Within the warm-core water, positive correlation also has been found, CH$_4$ production
and high CH$_4$-rich water, which was trapped when eddy formed. The positive AOU values here
may be caused by biological activities, CH$_4$ oxidation and remineralization of organic matters.
The present study indicates that eddies play a crucial role in controlling CH$_4$ distributions and
in transporting CH$_4$ laterally and nutrients as well.

CH$_4$ and N$_2$O concentrations in each water mass was examined. The highest CH$_4$ and
N$_2$O concentrations were simultaneously detected in the bottom water (PWW) of the shallow
Chukchi Sea where active microbial metabolism under low sedimentary oxygen condition
leads to high rates of CH$_4$ and N$_2$O production. Low CH$_4$ and N$_2$O in Atlantic-derived water
(AW) and subsurface Pacific-derived water (e.g., ACW and MW). Similar to CH$_4$, high N$_2$O
concentrations on the shelf water are transported through the Canada Basin. N$_2$O concentration
is used as supported data for CH$_4$ analysis. Both super-saturation and under-saturation of N$_2$O
were detected due to capacity of its sources and denitrification process in oxygenated water.

Sea-air fluxes of CH$_4$ were 1.02 (µmol m$^{-2}$ d$^{-1}$) and 2.4 (µmol m$^{-2}$ d$^{-1}$) that has been
measured by CRDS and GC measurement, respectively. They approximated to CH$_4$ fluxes of
the previous studies in the Chukchi Sea and southwestern Canada Basin. However, sea-air CH$_4$
flux is generally lower than that of in the East Siberian Sea or Barent Sea. I could not make a
comparison of sea-air CH$_4$ fluxes between within and outside the eddy because high CH$_4$
emission from the Chukchi Sea shelf to the atmosphere compared to the further region in the
southwestern Canada basin.

DMSP and chl-$a$ were considered as precursors of in situ CH$_4$ production during DMSP
degradation in oxygen-rich polar water and phytoplankton bloom, respectively. However, I
could not find the correlation between CH$_4$ and its precursors in this area. Therefore, CH$_4$ did
not produce from marine phytoplankton and methylated compounds (DMSP). High CH$_4$
production in the Chukchi Sea and southwestern Canada basin reflected by sedimentary
methanogenesis release.
Fig. 4.1 (a) Blue line shows the cruise track of R/V Mirai cruise (MR15-03 Leg. 1) from August to October 2015. Red box shows the area where the discrete CH$_4$ samples were taken. (b) Map of sampling stations of discrete seawater. Red line shows the transect crossing a warm-core eddy during the cruise.

Fig. 4.2 Vertical sections of potential temperature (°C) (color) and salinity (contours) (a); Brunt-Vaisala frequency (cph) (color) and potential density (contours) (b) from surface water to 200 m depth.
Fig. 4.3 The spatial distribution of CH$_4$ concentration (a-left) and CH$_4$ saturation (b-right) were measured by CRDS system in high latitudes in the Arctic Ocean.

Fig. 4.4 The spatial distribution of CH$_4$ concentrations at depths of 10 m (a), 50 m (b), and 200 m (c) corresponding to the water near the surface, within, and below the warm-core eddy at all stations during the cruise.
**Fig. 4.5** The vertical profiles of CH$_4$ concentration (left) and SR (right) eddy at whole stations during the cruise.

**Fig. 4.6** Salinity vs. temperature plot showing the different water masses observed in the southwestern Canada Basin. Circles indicate for dissolved CH$_4$. 
Fig. 4.7 The CH$_4$ flux in high latitudes in the Arctic Ocean from CRDS measurement during the cruise.

Fig. 4.8 Comparison of the vertical profiles of dissolved CH$_4$ concentrations in the southwestern Canada Basin inside (a) and outside of the warm-core eddy (b) from GC measurement.
**Fig. 4.9** Vertical transect distribution of CH$_4$ concentration was measured by GC following the red line of Fig. 4.1b. White background in both sides shows shelf area.
Fig. 4.10a Vertical transect distribution of ammonium (a), phosphate (b), silicate (c) concentration following the red line of Fig. 4.1b. White background in both sides shows shelf area.
Fig. 4.10b Vertical transect distribution of nitrate (d), fixed nitrogen (e) concentration and AOU (f) following the red line of Fig. 4.1b. White background in both sides shows shelf area.
Fig. 4.11 Plot of ammonium, phosphate, nitrate, N**, AOU and CH$_4$ against potential density ($\sigma_\theta$). Colorful dots indicate for data in each water mass.
Fig. 4.12 Comparison of the relation between CH$_4$ and ammonium, nitrate, phosphate and fixed nitrogen concentration within (yellow squares) and outside the warm-core eddy (blue squares).
Fig. 4.13 Chl-\(\alpha\) concentration (\(\mu\)g L\(^{-1}\)) integrated over the water column from the surface to a depth of 50 m (approximately the euphotic zone) for chlorophyll-\(\alpha\) in cells < 2 \(\mu\)m (blue bars), cells 2-10 \(\mu\)m (red bars), and cells > 10 \(\mu\)m (green bars). The coastal area was at the station 15, 30 and station 47; the warm-core eddy was at the station 37. Shelf-slope was at the station 23 and station 62.
Fig. 4.14 Comparison of the relation between methane and AOU between within (yellow) and outside (blue) the warm-core eddy. Black and red ellipsoid point out for the coastal stations and at the water-core eddy (100 m depth only), respectively.
Fig. 4.15 Comparison of the correlation between CH$_4$ and AOU (a) outside and (b) inside the eddy at isoline of 32 ($\sim$26$\sigma$) and N$^*$ minima.

Fig. 4.16 Vertical sections of N$_2$O concentration (nmol kg$^{-1}$) (color) and potential density (contours). White background in both sides shows shelf area.
Fig. 4.17 Salinity vs. temperature plot showing the different water masses observed in the southwestern Canada Basin during the cruise. Colorful circles indicate for dissolved N$_2$O concentration.
<table>
<thead>
<tr>
<th>Region</th>
<th>CH$_4$ concentration/Saturation</th>
<th>Flux (µmol m$^{-2}$ d$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>East Siberian Arctic shelves (ESAS)</td>
<td></td>
<td>70-450 nmol m$^{-2}$s$^{-1}$</td>
<td>Kosmach et al., 2015</td>
</tr>
<tr>
<td>ESAS</td>
<td>17.6 nmol L$^{-1}$; 5000%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ESS</td>
<td>229.375</td>
<td></td>
<td>Shakhova et al., 2010; Sapart et al., 2017</td>
</tr>
<tr>
<td>Barents and Kara Seas</td>
<td>10.5 nmol L$^{-1}$; 2200-2500%</td>
<td></td>
<td>Kosmach et al., 2015</td>
</tr>
<tr>
<td>Chukchi Sea &amp; Bering Sea</td>
<td>8.1 nmol L$^{-1}$; 1000%</td>
<td></td>
<td>Kosmach et al., 2015</td>
</tr>
<tr>
<td>Chukchi Sea</td>
<td>10.08</td>
<td></td>
<td>Li et al., 2017</td>
</tr>
<tr>
<td>Beaufort Sea shelf</td>
<td>8.75 – 26.87</td>
<td></td>
<td>Lorenson et al., 2016</td>
</tr>
<tr>
<td>Bering &amp; Eastern Chukchi Sea</td>
<td>4.8 nmol L$^{-1}$</td>
<td>1.9 ± 1.4</td>
<td>Fenwick et al., 2017</td>
</tr>
<tr>
<td>Central Arctic Ocean (ice-covered)</td>
<td>35</td>
<td></td>
<td>He et al., 2013</td>
</tr>
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</table>
Table 4.2 Observation of sea-air flux of CH$_4$ in the Arctic Ocean from the previous studies

<table>
<thead>
<tr>
<th>Region</th>
<th>Flux (µmol m$^{-2}$ d$^{-1}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>East Siberian Arctic shelves (ESAS)</td>
<td>70-450 nmol m$^{-2}$ s$^{-1}$</td>
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<td>Barents and Kara Seas</td>
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<td>Chukchi Sea &amp; Bering Sea</td>
<td></td>
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<td>Bering &amp; Eastern Chukchi Sea</td>
<td>1.9 ± 1.4</td>
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</tr>
<tr>
<td>Central Arctic Ocean (ice-covered)</td>
<td>35</td>
<td>He et al., 2013</td>
</tr>
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</table>

Table 4.3 Estimation of methane oxidation within the warm-core eddy with different oxidation rates.

<table>
<thead>
<tr>
<th>Oxidation rate (nM day$^{-1}$)</th>
<th>Initial CH$_4$ concentration (nmol kg$^{-1}$)</th>
<th>Expected CH$_4$ concentration over time (7 days)</th>
<th>References</th>
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<tr>
<td>0.0912</td>
<td>35.8</td>
<td>18.91</td>
<td>Kitidis et al., 2010</td>
</tr>
<tr>
<td>0.03-0.09</td>
<td>35.8</td>
<td>19.06 - 29.01</td>
<td>Savvicchev et al., 2007</td>
</tr>
<tr>
<td></td>
<td>35.8</td>
<td>32.30</td>
<td>This study</td>
</tr>
<tr>
<td>(at station 47)</td>
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CHAPTER 5:

CH$_4$ DISTRIBUTION IN SEA-ICE COVERED AREA IN THE ARCTIC OCEAN IN SUMMERTIME

5.1 Dissolved CH$_4$ under sea ice cover in the Arctic Ocean

Arctic region is the most vulnerable area to global warming (IPCC, 2007). A rate of ice loss in magnitude increased from $0.35 \times 10^6$ km$^2$ per decade during the period 1979-1993 (Comiso, 2006) to $0.9 \times 10^6$ km$^2$ per decade between 1993-2007 (Deser and Teng, 2008). According to Stroeve et al. (2012), the extent of sea-ice loss during summer has become remarkable recently, so the area of open water has increased in summertime. Decline in the Arctic sea-ice extent may affect changes in large-scale atmospheric circulation (Overland et al., 2008) and its chemical composition (Comiso, 2010). Sea-ice reduction accelerates light penetration into the ocean water, so it may enhance phytoplankton photosynthesis and supply foods for higher trophic level organisms. In the western Canada Basin, diatom productivity was greater in 2004 than in 1994; it implied that the biological pump was enhanced during 1994-2004 due to the sea ice retreat (Nishino et al., 2009). Sea ice acts as a physical barrier, and removal of this barrier directly affects the air-sea exchange of greenhouse gases as well as the exchange of energy and water (Bates et al., 2006; Loose et al., 2014). Sea ice completely prevent air-sea exchange in winter, and a closed sea ice cover may trap bubbles reaching the surface water. Characteristics of physical oceanography such as water masses, geography and biogeochemistry which influence on CH$_4$ distribution in the Arctic Ocean have been described in Chapter 4. Thus, in this chapter, additional information of CH$_4$ distribution especially in sea-ice cover region is added for further understanding.

Some previous reviews have compared CH$_4$ flux between ice-free and ice-covered regions. On the East Siberian Arctic shelf, CH$_4$ fluxes beneath the sea-ice cover (multi-year ice) are 2-10 times higher than in ice-free region (Shakhova et al., 2010; Kitidis et al., 2010). CH$_4$ fluxes in both ice-free region and ice-covered region range from 0.02 Tg CH$_4$ yr$^{-1}$ and 0.30 CH$_4$ yr$^{-1}$, respectively (Lorenson et al., 2016) in the Beaufort Sea. It suggested that accumulation of CH$_4$ under ice could enhance the annual sea-air flux due to CH$_4$ release after melting in seasonally ice-covered regions (Lammers et al., 1995). Increase of atmospheric CH$_4$ concentration has been detected over the open leads and regions with fractional sea-ice cover (Kort et al., 2012). During period of sea ice formation, gases are expelled from the sea-ice and
transported to the deeper layer or reached to the atmosphere while during summer melting ice dilutes the gas content of seawater (Anderson et al., 2004; Kitidis et al., 2010; Damm et al., 2015a).

Arctic continental shelves are well-known as “Arctic carbon hyper pool” refer to the huge content of organic carbon within the sedimentary basin (Semiletov et al., 2012). High level of CH$_4$ emission have been observed on the East Siberian Sea (Shakhkova et al., 2010) and in the upper continental slopes (Shakhkova et al., 2010; Ruppel and Kessler, 2017). The produced CH$_4$ from sediments could be transported by the ocean currents and diluted into the oceanic water. In the central Arctic, super-saturation of CH$_4$ in the oceanic water was also observed and is supposed to aerobic CH$_4$ production in the water column via degradation of DMSP (Damm et al., 2010). Sea ice is a DMSP-rich water where abundance of precursors of CH$_4$ in the polar water. Sea ice processes have been identified as potential CH$_4$ sources associated with microbial activities in anoxic brine channels (Damm et al., 2015a). The sea ice zone could biologically produce CH$_4$ with depleted nitrate and available phosphate (Karl et al., 2008; Damm et al., 2010). A low N:P ratio enhances the ability of bacteria to compete for phosphate while the phytoplankton metabolite DMSP is utilized as a C source. During this process, methyl-phosphonate is converted into CH$_4$ without requiring anoxia (Karl et al., 2008). Hence, there are potentially important CH$_4$ cycle processes in the sea ice zone, however, relation of CH$_4$ with sea ice is not clear at this stage.

Most of studies on CH$_4$ emission in Arctic Ocean focused on shelf areas whereas the central Arctic Ocean has rarely been investigated (Damm et al., 2010; 2015) as a result of long-term ice cover. The effect of reduced sea-ice cover may affect the amount of CH$_4$ emission into the atmosphere. There are not as much as investigations on the CH$_4$ distribution in the sea ice covered area. The role of CH$_4$ distribution under sea ice cover has not been understood completely yet, thus comprehension of this role is needed to investigate to understand the gas exchange between sea-ice and atmosphere in the Arctic Ocean. In this study, I investigated CH$_4$ flux from the southern Bering Sea crossing the Chukchi Sea shelf to central Arctic Ocean under two conditions: beneath sea-ice cover and sea ice-free regions. This allowed us to gain some insights into the role of sea ice on CH$_4$ emission and budget of CH$_4$.

5.2 Experimental Setting

During the period of August 2016, seawater samples were collected from IBRV **ARAON** cruise (ARAON-07B) throughout the water column. The majority of sampling was conducted
over the Bering Sea, Chukchi Sea and Arctic Ocean (Fig 5.1) during the cruise in order to investigate the vertical profiles of dissolved CH$_4$ in the Arctic Ocean under ice-free region and sea-ice cover region. Vertical seawater samples were taken using 24 Niskin bottles (12L) mounted on a rosette, were used to make observation at 31 stations. At each station, a Sea-Bird CTD system (SBE 911+) equipped with ancillary sensors was used to measure salinity, temperature, and other hydrographic parameters. Over 130 seawater samples were collected for CH$_4$ analysis at 21 stations with various depths (from surface seawater to the bottom water). CH$_4$ samples have been measured by GC-IRMS and description of GC system has been mentioned in Chapter 2. Approximately 190 seawater samples for each DMS, DMSPp, and DMSPt were also collected at 31 stations from surface to about 300 m depth. DMS samples was immediately measured on board as soon as possible after sampling. DMSP samples were treated by adding acid solution (see Chapter 2) and stored in a dark place at room temperature. These samples were measured by GC-FPD on land at Hokkaido University, and description of GC-FPD measurement has also been described in Chapter 2.

This research aims to examine the vertical profiles of CH$_4$ and DMSP distribution in Bering and Chukchi Sea (coastal and ice-free region) and the central Arctic Ocean (beneath sea-ice). The cruise crossed main distinct water masses influenced by a range of physical and biological processes that impact salinity, temperature, and nutrients concentrations, such as PSW, PWW, ACW, MW, and AW (these water masses are mentioned in Chapter 4). An available CH$_4$ emission above seafloor sediments and comparison of CH$_4$ distribution between ice-free region and sea-ice cover region were investigated.

The atmospheric concentration of CH$_4$ was assumed as 1850 ppb, based on the average mixing ratios in Barrow, Alaska in 2015 (Data provided by NOAA ESRL Global Monitoring Division, Boulder, Colorado, USA). Weekly sea-ice concentration was downloaded from National Oceanic & Atmospheric Administration (NOAA), which was produced on 1°x1° grid (https://www.esrl.noaa.gov/).

5.3 Results and Discussion

5.3.1 Dissolved CH$_4$ distribution in the water column

Over the region, the dissolved CH$_4$ concentration ranged from 3.5-23.1 nmol kg$^{-1}$ and the average was 7.5 nmol kg$^{-1}$ in the surface seawater (at 0 m depth) (Fig 5.2a). Dissolved CH$_4$ was ubiquitously supersaturated (range: 124.7-604.6%; average: 216%) in the surface seawater
(Fig 5.4b) respecting to atmospheric CH$_4$ concentration. The highest CH$_4$ oversaturation were 605% (23.1 nmol kg$^{-1}$) in surface water at Chukchi sea shelf (sta #12).

At the Bering Sea and Chukchi Sea shelf, CH$_4$ concentration increased with depth to the bottom from station #1 to station #13. At the shelf break, CH$_4$ concentration was as high as 38.94 nmol kg$^{-1}$ (SR = 1019%), approximately 7 times higher than surrounding surface water (5 nmol kg$^{-1}$; SR ~150%) (Fig 5.4). Away shelf water, at a few stations with depth greater than ~200 m, the CH$_4$ concentration increased with depth up to 50-10 m depth but decreased with greater depths. The lowest CH$_4$ concentration at 200 m was 0.96 nmol kg$^{-1}$ (SR = 27%).

High CH$_4$ supersaturation appeared in bottom water above sediment. Water contains SR of 1019% (38.94 nmol kg$^{-1}$) probably resulted from high in situ methanogenesis with organic matter in the sediment layer (Reeburgh, 2007) and then diffused the produced CH$_4$ into the water column. High CH$_4$ concentration at the shelf slope (station #12) was also observed (Li et al., 2017) with high organic matter settling over bottom layer (Nishino et al., 2005). Maximum CH$_4$ (35.8 nmol kg$^{-1}$) concentration upper the bottom water (sta. #12) in our observation was higher than that of Kudo et al. (2017) (20 nmol kg$^{-1}$) at the same position. Methanogenesis rate in the sediment of the Chukchi Sea was up to 67 µmol m$^{-2}$ d$^{-1}$ (Savvichev et al., 2007), implying that it may be a major source of CH$_4$ releasing into the water column.

Further the shelf slope, CH$_4$ concentration increased up to SCM layer (~40 m) and decreased with depth until the bottom. The lowest CH$_4$ value of 0.96 nmol kg$^{-1}$ (SR = 27%) at the deeper water. High CH$_4$ concentrations were above 100 m depth at a distance of 3000 km of transect may be transported to the northern Arctic by northward flowing of ocean currents of (e.g., ACW (Watanabe et al., 2014) or Anadyr water (AnW) with CH$_4$ concentration of 10.11 nmol kg$^{-1}$ (SR = 277.5%). At a distance of 1500 km of the transect, a plume of CH$_4$ was observed, which might be derived from East Siberian Coastal Water where high CH$_4$ concentration was observed (Shakkhova et al., 2005).

5.3.2 Dissolved CH$_4$ in distinct water masses

Dissolved CH$_4$ concentration varied in different water masses. In this study, observed CH$_4$ concentrations were lower in Atlantic-derived water (AW) than in Pacific-derived water (Pdw, including PSW, PWW, ACW) (Fig 5.3b). The ACW contained high inputs of CH$_4$ from riverine water before it enters the Chukchi Sea and the Arctic. High CH$_4$ in the river water reflects the methanogenesis of organic matter in degrading permafrost (Striegl et al., 2012). On the other hand, Ruppel (2015) reported that subsea permafrost or gas hydrate did not affect the
elevated CH$_4$ here. This observed CH$_4$ concentration is consistent with the observation of Fenwick et al. (2017) and Li et al. (2017). In MW, CH$_4$ concentration was relatively medium and was less than 10 nmol kg$^{-1}$ excepting for a few points. CH$_4$ concentration is high in PWW (cold and saline) that is suggested by a brine rejection process in the winter. This process causes convective overturning and mixes up from the sediments, releasing regenerated nutrients and gases into the PWW (Pickart et al., 2016). Therefore, methanogenesis in the sediments may contribute to the high CH$_4$ concentration in the PWW and ACW.

Fig 5.5 shows CH$_4$ concentration was negatively correlated with sea water temperature, especially in the ACW (CH$_4$ = -1.585×Temp + 19.92, $R^2 = 0.51$, n = 36). This correlation explains high-CH$_4$ water in warmer water where derived river water containing high CH$_4$ production. Near the bottom-colder water or in the PWW (yellow circles), CH$_4$ concentration focused on at the cold water temperature, which derived from mixing of CH$_4$-bottom water on the shallow shelf water. In the cold water, temperature did not limit the production and emission of CH$_4$ was suggested in early research. In contrast, MW including meltwater and river water contained relatively high CH$_4$ concentration (5-10 nmol kg$^{-1}$) but there was no correlation between them.

No correlation between CH$_4$ concentration and salinity in whole water column has been found (Fig 5.6) compared to its correlation in each water mass. However, CH$_4$ looks like positively correlated to salinity in the MW; it will be discussed later on.

5.3.3 Sea surface CH$_4$ distribution in open water and sea ice cover region

Sea-ice presents as a barrier for restriction at sea-air interface and variation in the sea-air flux of CH$_4$ (Loose et al., 2014). In summer when sea ice melting, CH$_4$ from temperature destabilization of gas hydrates on the continental shelf (Westbrook et al., 2009) and trapped CH$_4$ gas beneath sea-ice can release into the atmosphere.

Basing on distribution of sea ice coverage, I divided research area into two sub-regions: shelf water and sea ice cover region. Shelf water covered from station #1 to station #11 and station #16. Especially, CH$_4$ plume on the shelf water includes the stations from #3-8. Sea ice cover region was the rest of stations, including CH$_4$ plume at station #12. The averaged CH$_4$ in the shelf water was lower than in sea ice cover region with concentration of 6.06 nmol kg$^{-1}$ (SR = 199%) and 7.38 nmol kg$^{-1}$ (SR = 231%) (excluding station #12), respectively (Fig 5.7). In this study, two assumptions of CH$_4$ supersaturation in the sea ice cover is supposed as follows:
(1) CH₄ plume originating from nearby sediments was advected or mixed up into the water column and then the CH₄ was accumulated under sea-ice (Kitidis et al., 2010; Lorenson et al., 2016) or

(2) Due to mineralization of organic matters derived from sea ice algae (Rysgaard and Glud, 2004) which can act as a substrate for methanogenesis. Methanogenesis is detected during zooplankton grazing (DeAngelis and Lee, 1994) and phytoplankton blooms (Damm et al., 2008).

Not only those, high CH₄ was also observed under a multi-year sea-ice or in the marginal ice zones (MIZ) (Kitidis et al., 2010) implying that sea ice cover could influence the exchange of CH₄ between seawater and air. Appearance of sea ice directly influences on seawater temperature and salinity. Due to high CH₄ concentration in the sea ice cover, the correlation between CH₄ and SST at surface seawater is considered. No clear correlation between them was found at the shelf water (blue circles) but CH₄ concentrated at low sea water temperature in the sea ice cover (red squares) (see Fig 5.8).

The difference in salinity responses to CH₄ concentration results in different local sources of CH₄ (Yoshida et al., 2011; Fenwick et al., 2017) in surface seawater. In this study, CH₄ concentrations was positively agreed to sea surface salinity (SSS) (Fig 5.9) with two distinct correlations. In the shelf water, the positive correlation is found (CH₄ = 2.92×SSS – 86.02, R² = 0.6, n = 10) at SSS was higher than 30 (30-33‰) which contains the Pacific-derived water and CH₄ sources is suggested from methanogenesis of organic matter. The produced CH₄ upper sediments is stirred up with higher salinity by vertical mixing. Then it was dispersed and diluted in the water column. In the sea ice cover region, I found the positive correlation between CH₄ and SSS (CH₄ = 1.14×SSS – 25.45, R² = 0.68, n = 9) at SSS was lower than 30 (‰), meaning fresh and low density surface water. CH₄ was generally supersaturated in this water. In this region, low salinity water may result from rivers or ice melting. Rivers input could also be supplied CH₄ from methanogenesis in sediments Chukchi sea shelf at higher salinity whereas at lower salinity CH₄ could be supplied from ice melting. Because sea ice contains anaerobic brine channels, which can contain high concentration of CH₄ due to decomposition of organic matter (Damm et al., 2015). CH₄ from open water region is transported and then is accumulated beneath sea-ice is immediately released when sea ice cracked (Damm et al., 2015b). In recent, sea ice contains rich-DMSP water (Asher et al., 2011; Stefels et al., 2018) especially sea ice melting directly impacts DMS(P) distribution. As the sea ice begins to melt, this brine extracts into the surface layer of the ocean. Observed CH₄ belongs to MW water mass including river
water and melting water (Fig 5.9). The slope is greater at the shelf water than in the sea-ice cover, implying that CH$_4$ production is faster at higher salinity than at low salinity. However, Fenwick et al. (2017) have been observed inverse correlation between CH$_4$ and salinity at the Canadian Arctic Archipelago. The supersaturated CH$_4$ observed in the surface water could be produced in local melting of sea ice as Damm et al. (2015a) suggested methane excess in Arctic surface water enhanced by sea ice formation and melting. This study is generally consistent with Damm et al. (2015b) that sea ice acts as a CH$_4$ source and a semi-permeable barrier to sea-air.

5.3.4 Correlation of CH$_4$ and nutrients in seawater

The Arctic Ocean water comprises both low salinity, nutrient-rich water and relatively nutrient-poor, more saline water (Pabi et al., 2008). In the Chukchi Sea shelf, high ammonium concentration is produced during summer by decomposing of organic matter at the place where high organic matter is deposited at the bottom (Nishino et al., 2005). The correlation between CH$_4$ and nutrients is collected at 0-50 m depth.

In summer, chl-$a$ concentration increased approximately at the Bering and northern Chukchi sea shelf with the maximum greater than 7.0 mg m$^{-3}$. The correlation between CH$_4$ and chl-$a$ in the shelf water was not found ($CH_4 = 11.19 \times $chla + 6.41, $R^2 = 0.48$) so strongly as in the sea ice cover region ($CH_4 = 4.82 \times $chla + 6.10, $R^2 = 0.48$).

Over the shelf-water, high ammonium concentration increased at the bottom (5.8 $\mu$mol kg$^{-1}$) (Fig 5.11) while ammonium concentration was low (~0 $\mu$mol kg$^{-1}$) in high latitudes. This implied that high ammonium concentration could be expected high organic matter and produced CH$_4$ through methanogenesis by decomposing of organic matter in anoxic sediments. Thus, the correlation between ammonium and CH$_4$ was found ($CH_4 = 3.09 \times $NH$_4$ + 9.52, $R^2 = 0.65$) at the shelf water (Fig 5.12) and in the sea-ice cover region ($CH_4 = 12.38 \times $NH$_4$ + 13.90, $R^2 = 0.55$).

Bering and Chukchi water derive water of Pacific which is continuously depleted in nitrate relative to phosphate (Yamamoto-Kawai et al., 2006). Nitrate + nitrite concentrations increased with depth. Unfortunately, there was not data of nitrate and nitrite separately. Total concentration were maximum at the shelf slope (1000 km distance of the transect) approximately 18 $\mu$mol kg$^{-1}$ (Fig 5.11). The correlations between CH$_4$ and total nitrate + nitrite concentration were found due to the existence of nitrite in the shelf water and ($CH_4 = 9.63 \times ($NO$_2$ + NO$_3$) + 9.33, $R^2 = 0.65$) and in the sea ice cover region ($CH_4 = 1.36 \times ($NO$_2$ +
NO\textsubscript{3}) + 8.11, R\textsuperscript{2} = 0.87). Nitrate + nitrite concentration in the sea ice cover was generally lower than in the shelf water. For phosphate, at the shelf water phosphate concentration was as high as \(\sim2.5 \, \mu\text{mol kg}^{-1}\) upper the sedimentary layer and further offshore phosphate was high at around 100 m depth (Fig 5.11). The positive relationships between CH\textsubscript{4} and phosphate were found at the shelf water (CH\textsubscript{4} = 24.19×PO\textsubscript{4} – 2.35, R\textsuperscript{2} = 0.81) and in the sea ice cover region (CH\textsubscript{4} = 14.89×PO\textsubscript{4} – 1.5, R\textsuperscript{2} = 0.87) (Fig 5.12). Tight correlations between CH\textsubscript{4} and phosphate in both regions mean that excess phosphate is available for bacterial biomass production produced DMSP and possible source to produce CH\textsubscript{4} biologically. Phosphate availability may influence the utilization of DMSP and produce CH\textsubscript{4} as a precursor (Damm et al., 2008; 2010). Relation between CH\textsubscript{4} and DMSP concentration should be considered.

In the surface layer, low nitrate concentration is probably attributable to the inflow of Bering shelf water with relatively low N\textsuperscript{**} values and the biological utilization during the inflow of the Pacific water into the Arctic Ocean through Bering Strait. A broad continental shelf of Bering and Chukchi Sea is denitrification sites, and minimum values of N\textsuperscript{**} was observed (Codispoti et al., 2005a; Gruber and Sarmiento, 2009). In particular, minima N\textsuperscript{**} (-17.9 \, \mu\text{mol kg}^{-1}) correlated to maxima nutrients of PO\textsubscript{4}\textsuperscript{3−}: 2.51 \, \mu\text{mol kg}^{-1} (Fig 5.13) at the shelf slope where CH\textsubscript{4} concentration was maxima. The similarity of minimum N\textsuperscript{**} results in the Bering, Chukchi sea shelf water, and further Arctic has been reported at the same depth (Devol et al.; 1997; Yoshikawa et al., 2006; Hirota et al., 2009; Hioki et al., 2014).

Apparent oxygen utilization (AOU) was high (> 151 \, \mu\text{mol kg}^{-1}) (Fig 5.11) near the bottom layer at the shelf slope indicated low dissolved oxygen (DO) concentration even though it still maintained aerobic biological activities. High CH\textsubscript{4} was obtained at high AOU that indicates anaerobic environments where CH\textsubscript{4} could be released from the sediment into the water column. There were no clear correlations between AOU and CH\textsubscript{4} at the shelf water and in the sea ice cover region in the whole region. However, in the CH\textsubscript{4} plume on the shelf water near Point Hope, CH\textsubscript{4} relatively correlated to AOU (CH\textsubscript{4} = 0.096×AOU + 14.59, R\textsuperscript{2} = 0.6) at the station #2-7 whereas it scattered at the Chukchi shelf slope station #12. In contrast, at the station #18 and #19 this water contains high CH\textsubscript{4} and negative AOU. At the negative AOU, it was not a condition for producing CH\textsubscript{4}, so the CH\textsubscript{4} may be resulted in water mixing derived from the East Siberian Sea before arriving here. In short, CH\textsubscript{4} relatively correlated with nutrients, especially with phosphate within Pacific-derived water. High concentrations of CH\textsubscript{4} at the shelf water were consistent with high organic matter settling above the sea bed.
5.3.5 Distribution of Nitrous oxide (N\textsubscript{2}O)

Nitrous oxide concentration in the Arctic Ocean ranged from 8.5 to 78.9 nmol kg\textsuperscript{-1} (Fig 5.14). In surface water, N\textsubscript{2}O concentration was almost supersaturated (range: 51.6-633.7%, averaged saturation: 132%) respecting to atmospheric N\textsubscript{2}O, with maximum concentration up to 21.4 nmol kg\textsuperscript{-1} (Fig. 5.5). High N\textsubscript{2}O concentrations were at the Chukchi Sea shelf averaging of 140-150% saturation whereas higher N\textsubscript{2}O concentration (~400%) (or N\textsubscript{2}O “hotspot”) from East Siberian Sea might be transported into this region by lateral transport observed at the stations #18 and #19 due to no existence of high N\textsubscript{2}O at the bottom water. At deeper water, N\textsubscript{2}O decreased with depth (> 200 m) and was under-saturated (~50% saturation) comparing to shallow water. This observation is relatively higher than the recent observation of Zhan et al. (2015) and Fenwick et al. (2017), who reported an average dissolved N\textsubscript{2}O concentration of 12.5 and 13 nmol kg\textsuperscript{-1} in the same region, respectively. N\textsubscript{2}O concentrations were similar to the previous observations of Fenwick et al. (2017) and Kitidis et al. (2010). N\textsubscript{2}O saturation at the shelf slope (123%) was higher in the sea ice cover (112%).

\[ \Delta \text{N}_2\text{O} \] is determined by difference between observed N\textsubscript{2}O and equilibrium N\textsubscript{2}O concentrations. In this study, positive \( \Delta \text{N}_2\text{O} \) located on the negative N\textsuperscript{+} implied the N\textsubscript{2}O productions through denitrification in this region. Zhang et al. (2015) and Fenwick et al. (2017) strongly suggested that the N\textsubscript{2}O production from the sediment of the Bering Sea and Chukchi Sea are a primary source in the Arctic Ocean. However, the positive \( \Delta \text{N}_2\text{O} \) concentration was at the positive N\textsuperscript{+} shows not only denitrification work as a N\textsubscript{2}O source in Atlantic origin water.

5.3.6 DMSP and Precursor of CH\textsubscript{4} in the Arctic

5.3.6.1 Distribution of total DMSP (DMSPt), DMSPd and DMS concentrations

During the cruise in summer (August 2016), high DMSPt concentrations were observed in the Chukchi Sea ranged from 0 - 90.8 nmol L\textsuperscript{-1} in the whole region with an averaging of 8.2 nmol L\textsuperscript{-1}. At the depth of about 250-300 m depth, DMSPt concentration is very low and almost zero. DMS concentration ranged from 0 to 8.87 nmol L\textsuperscript{-1}, averaging of 0.71 nmol L\textsuperscript{-1} from surface seawater to about 300 m depth. In the surface water, DMS concentration ranged from 0.195 to 7.99 nmol L\textsuperscript{-1} with an averaged value of 1.27 nmol L\textsuperscript{-1}. In this observation, high DMS concentration in the Chukchi Sea shelf was up to 8.87 nmol L\textsuperscript{-1}. DMS concentration from our observation is lower than that of Sharma et al. (1999) in off Alaskan Coast and western Canada Basin (range: 2-23 nmol L\textsuperscript{-1}, average: 12.1 nmol L\textsuperscript{-1}). High DMS concentration over there is caused by high productive shelf region (Gosselin et al., 1999) as well as high organic matter
settling (Nishino et al., 2005). DMSP may convert into DMS in the water column via photochemical and bacterial processes (Kiene et al., 2000; Stefels et al., 2007) and produce another product as dimethylsulphoxide (DMSO).

In the water mass in the Arctic, high DMS concentration lied in the warmer and less saline water ($T > 0{^\circ}C$, $S = 31-33 \text{‰}$) or Pacific-derived water (Fig 5.17; Fig 5.18; Fig 5.19) whereas low DMS concentration located on the cold water such as AW, PWW, and MW. In addition, sea surface DMSPt generally increased to sea ice concentration, but DMS varied in the sea ice cover region (Fig 5.20). High concentration of DMSPt at the sea ice cover has been reported by Asher et al. (2011) and Brabant et al. (2011).

5.3.6.2 Precursors of DMSP

DMSP is one of the methylated compounds produced by variety of marine phytoplankton (Keller et al., 1989). DMSP plays a significant role in marine surface water (Kiene et al., 2000) because of DMSP accounting for 1-10% of total phytoplankton carbon. Thus, the correlation between DMSP and chl-$\alpha$ concentration is needed to examine in the polar mixed water (<50 m depth). High DMSPt concentrations were consistent with degradation of chl-$\alpha$ concentration over shelf water whereas DMSPt concentration increased with enhancement of chl-$\alpha$ concentration in the sea ice cover region (Fig 5.21; Fig 5.16). Weak negative correlation between DMSPt and chl-$\alpha$ concentration was found in the shelf water ($R^2 = 0.28$), while tighter positive correlation was stronger in the sea ice cover ($R^2 = 0.65$) even though those concentration is smaller 3-4 times than that of in the open water. Observed chl-$\alpha$ may result from ice melting release when trapped in ice formation in winter. Phytoplankton growth is restricted to the short melting period in spring and summer in a seasonal ice cover. At the ice edge zone (IEZ), region of seasonal melting is known as an area of intensive biological activity (Smith and Nelson, 1985).

DMS in the surface mixed layer is exposed to removal processes includes photochemical oxidation, micro-biological degradation, ventilation to the atmosphere, advection and vertical mixing. DMS in surface water appears to be primarily controlled by the biological cycle of DMS and DMSP (Kiene and Bates, 1990; Leck et al., 1990). Global DMS estimation from the ocean range from 250-1600 Gmol S yr$^{-1}$ (Spiro et al., 1992), which accounts for about 50% from ocean, plants, and soils (Bates et al., 1992).
5.3.6.3 Precursor of CH$_4$

Over the shelf water, high DMSP, chl-\textit{a} (>2 mg m$^{-3}$) and CH$_4$ concentrations were observed near the CH$_4$ hotspot. Phytoplankton is believed to be a main source of DMSP and DMS (Challenger and Simpson, 1948) and CH$_4$ (Damm et al., 2008) in the ocean as well. Kudo et al. (2018) suggested DMSP as a source of CH$_4$ in the Arctic Ocean. In the shelf water, DMSPt degradation correlated to CH$_4$ production except for the stations high CH$_4$ release upper the sedimentary layer. It is shown in the negative correlation between CH$_4$ and DMSPt (CH$_4$ = -0.52×DMSPt +25.9, $R^2$ = 0.58) (Fig 5.22a). The finding equation implies that CH$_4$ production increased when DMSPt degraded. \textit{In situ} excess here CH$_4$ could produced during the phytoplankton bloom while DMSP and its degradation products acts as potential source for CH$_4$. The degree of oligotrophic water in the Arctic and the decreasing DMSPt concentration reflect an increasing utilization of DMSP as a carbon source (Damm et al., 2010). In contrast, in the sea-ice cover region a positive correlation between CH$_4$ and DMSPt (CH$_4$ = 0.44×DMSPt + 5.38, $R^2$ = 0.67) indicates that increase in CH$_4$ production correlated to increase in DMSPt production (Fig 5.22b). The two correlations between and CH$_4$ and DMSPt concentration reflect two different potential sources of CH$_4$ over Chukchi Sea shelf water containing high nutrient concentrations and organic matters and in the sea ice cover. The excess phosphate water and the presence of sea ice ability (see section 5.3.3) influence on DMSPt production and CH$_4$ production as well. Thus, in the sea ice cover region, both sea ice and DMSPt work as \textit{in situ} potential CH$_4$ sources.

5.4 Summary and Conclusion

CH$_4$ distribution in the Arctic Ocean was investigated under two conditions: in the shelf water and sea ice cover region in order to evaluate the influence of sea ice coverage on CH$_4$ contribution and CH$_4$ emission. During the cruise of R/V ARAON (ARAON-07B) in the Arctic Ocean in summer 2016, seawater samples of CH$_4$ from the surface seawater to the bottom were collected and analyzed. CH$_4$ was obviously supersaturated in the surface water over the region from 124-604%. High CH$_4$ concentration (1019%) was observed in the Chukchi shelf water close to CH$_4$ hotspot release from the anaerobic environment in sediments into the water column, which is linked to the positive AOU upper. The correlations between CH$_4$ and ammonium, nitrite+nitrate, phosphate and N$^{**}$ concentration reflect the high CH$_4$ production co-existence to high organic matter. Beneath the sea-ice cover region at deeper water (> 200 m depth), low CH$_4$ concentration in deep water was controlled by CH$_4$ oxidation in aerobic
environmental water. CH$_4$ characteristic is clearly different in each water mass (ACW, PSW, PWW, MW, AW).

In the sea ice cover, surface seawater CH$_4$ concentrations in the sea ice were lower than that of over the shelf water. High CH$_4$ at surface seawater in the sea ice cover may be trapped by northward flowing into the Arctic Ocean advected and accumulated under sea ice cover. On the other hand, mineralisation of organic matter in sea ice brine channel can supply for producing CH$_4$ inside sea ice and expel into seawater or the atmosphere when ice melting. However, CH$_4$ generally increases with sea ice concentration suggests CH$_4$ can be produced in local melting or formation of sea ice. This study clarifies sea ice act as the semi-permeable barrier to sea-air exchange.

DMSP and CH$_4$ production is directly affected by phytoplankton bloom, which is presented by chl-$a$ concentration, was considered as their sources. DMSP is examined as the precursor of CH$_4$ with the two distinct correlations under two conditions was found. I supposed that DMSP is considered to be a precursor of CH$_4$ in the Arctic Ocean and directly affect to amount of CH$_4$ emission into the atmosphere, especially in the sea ice cover region.

High N$_2$O near the bottom water in the Chukchi shelf water and existence of N$_2$O “hotspots” in the sub-surface water and off-shore water originated with lateral transport from East Siberian Sea or a branch of Anadyr Water with remarkably high N$_2$O concentration because “hotspots” of N$_2$O did not link to the bottom water. The N$_2$O data is used to trace out the mechanism of CH$_4$ sources and transport.
Fig 5.1 Sampling stations of cruise track of IBRV ARAON (ARAON-07B) on August 2016 in the Arctic Ocean. Discrete seawater samples is shown in red circles. Sea ice concentration (%) is shown in white. This figure is plotted by Ocean Data View.

Fig 5.2 The spatial distribution of CH$_4$ concentration (nmol kg$^{-1}$) (a) and CH$_4$ saturation (%) (b) in surface water in the Arctic Ocean during the cruise of IBRV ARAON (ARAON07B) August, 2016. The figure is plotted by Ocean Data View.
Fig 5.3 (a) Oceanic currents in the Bering, Chukchi and Arctic Ocean (Source: http://research.cfos.uaf.edu/nprbdrifters/). (b) Salinity vs. potential temperature plot showing the different water masses observed in the Arctic Ocean. Figure shows CH$_4$ concentration. This figure is plotted by MATLAB.
Fig 5.4 Vertical transect distribution of temperature (°C), salinity (‰) and dissolved CH$_4$ concentration following in order stations (1-31).
Fig 5.5 Plot of CH$_4$ concentration versus temperature within each water masses in the Arctic Ocean (AW, PWW, PSW, ACW, MW).
Fig 5.6 Plot of CH$_4$ concentration versus salinity within each water masses in the Arctic Ocean (AW, PWW, PSW, ACW, MW).

Fig 5.7 The distribution of CH$_4$ concentrations in the shelf water and in the sea ice cover region.
Fig 5.8 Plot of CH$_4$ concentration versus SST in the shelf water (blue circles) and sea-ice cover region (red-squares).
Fig 5.9 Plot of CH$_4$ concentration versus salinity in the shelf water (blue circles) and sea-ice cover (red-squares).
Fig 5.10 Correlation between CH$_4$ and sea ice concentration in the sea ice cover region.
Fig 5.11a Vertical transects of distribution of (a) chl-α; (b) Ammonium; (c) nitrate and nitrite; (d) phosphate; (e) silicate; (f) fixed nitrogen (N\textsuperscript{+}); (g) Dissolved Oxygen (DO); (h) AOU concentrations following in order stations (1-31).
Fig. 5.11b Vertical transects of distribution of (a) chlorophyll-a; (b) Ammonium; (c) nitrate and nitrite; (d) phosphate; (e) silicate; (f) fixed nitrogen \(\text{N}^{\text{**}}\); (g) Dissolved Oxygen (DO); (h) AOU concentrations (to be continued) following in order stations (1-31).
Fig 5.12 The correlation between CH$_4$ and chl-$\alpha$, ammonium, total dissolved (nitrite + nitrate) and phosphate concentration over the shelf water region and sea ice cover region.
**Fig 5.13** Correlations between CH$_4$ and N$^{**}$ over the shelf water region and sea ice cover region.

**Fig 5.14** Vertical distribution of nitrous oxide (N$_2$O) during the cruise following in order stations (1-31).
Fig 5.15 Vertical transects of distribution of (a) dimethyl sulphide (DMS); (b) dissolved dimethyl sulphide (DMSPd); (c) total dimethyl sulphide (DMSPt) during the cruise.
Fig 5.16 DMSPt (upper panel) and DMS (bottom panel) concentration in surface water in order of stations in the Arctic Ocean during the cruise.
Fig 5.17 Salinity vs. potential temperature plot showing the different water masses observed in the Arctic Ocean. Figure shows DMS and DMSPt concentrations. This figure is plotted by MATLAB.
Fig 5.18 Plot of DMS Pt and DMS versus seasurface salinity (SSS)

Fig 5.19 Plot of DMS Pt and DMS versus seasurface temperature (SSS)
**Fig 5.20** Plot of DMSPt and DMS versus sea ice concentration

**Fig 5.21** Plot of DMSPt versus chl-a concentration in the shelf water (left panel) and in the sea-ice cover region (right panel). Black line shows regression line between DMSPt concentration and chlorophyll a concentration.
Fig 5.22 CH$_4$ and DMSPt concentration in the shelf water (left panel) and in sea-ice cover region (right panel). Black line shows regression line between methane concentration and chlorophyll a concentration.
CHAPTER 6: GENERAL CONCLUSION

6.1 Conclusions of this study

In this study, I examined the CH₄ distribution in seawater in the polar regions and investigated the controlling factors including physical and biological factors affect CH₄ distribution. The continuous mixing ratios of CH₄ was measured by new continuous measurement system (CRDS) coupling with an equilibrator. Discrete dissolved CH₄ was measured by GC – IRMS. This observations have provided the dissolved CH₄ distributions under the effects of controlling factors and amount of CH₄ efflux from the ocean to the atmosphere.

Obtained high-resolution CH₄ data in the polar waters (Chapter 3, 4) aims to reduce less uncertainties in estimation of CH₄ flux and supports for research of CH₄ (Chapter 3, 4, and 5). Controlling factors is considered including physical factors and biological factors. Physical factors include the vertical mixing (Chapter 3), eddies transport and lateral transport (Chapter 4), and physical barrier of sea ice cover (Chapter 5). The finding negative relationship between SR and AOU points out the vertical mixing and upwelling in shallow areas supplies poor-CH₄ water from deeper water to surface water in the Southern Ocean and influences on the spatial distribution of CH₄ (Chapter 3). Lateral transport and warm-core eddies play a role in transporting CH₄ from the shelf water into the Arctic/Canada basin. Eddies plays a key phenomenon in transporting and contributing to dissolved CH₄ both in horizontally and vertically (Chapter 4). Achieved results have shown combination of biological and physical factors influence on dissolved CH₄ distribution. However, further research would be required to elucidate the difference in lateral transport and transport of warm-core eddies.

In addition, biological parameters was mentioned such as components of inorganic nutrients, chl-a indicating for abundance of organic matter settling upper the sediments producing CH₄ through methanogenesis in anaerobic environment (Chapter 4, 5). As a result, the negative correlation between SR and AOU is examined in the Arctic Ocean shows CH₄ is generally oxidized in the aerobic water column except for producing CH₄ showing in the positive correlation. The results indicate that high CH₄ production were at negative AOU while CH₄ oxidized at the positive AOU both in the Southern Ocean and in the Arctic Ocean (Chapter 3, 4). In fact, it is hard to determine the limitation of AOU co-existence with CH₄ production. Moreover, significant correlation between SR and AOU was observed in the Southern Ocean suggesting that it would be useful for estimating CH₄ flux from AOU data directly.
As if sea ice coverage prevent sea-air exchange, observed high CH$_4$ when sea ice cracking may accumulated of northward flowing water beneath sea ice. Mineralisation of “regenerated” organic matter in brine channel can supply for methanogenesis and then release into seawater or the atmosphere when ice melting. In contrast, appearance of sea ice could be enhanced CH$_4$ exchange at sea-air interface that is expressed via the positive correlation between CH$_4$ and sea ice concentration. Salinity could be a key factor controlling CH$_4$ distribution because CH$_4$ can be produced in local sea ice formation or ice melting. Sea ice acts as semi-permeable barrier to CH$_4$ sea-air exchange (Chapter 5).

These results obtained from this study elucidate distinct factors impact the spatial distribution of CH$_4$ between the Southern Ocean and Arctic Ocean as well as in the shelf water...
and in the sea ice cover region. It would contribute to the future observation of CH$_4$ emission from the ocean to the atmosphere.

6.2 Possible feedback to climate change

The present study demonstrated that the controlling factors influence on the dissolved CH$_4$ distribution in the polar regions. Climate change can affect ocean biogeochemical cycles, ocean water masses, sea ice cover, CH$_4$ emission from the ocean surface and create a feedbacks to climate. Upwelled high AOU level in recent would raise up the poor CH$_4$ water and then prediction of the contribution of CH$_4$ emission from surface seawater in the Southern Ocean would reduce. In contrast, the Arctic is the most sensitive to climate change presenting increase in seawater temperature and melting of sea ice. Reducing in sea ice cover on the permafrost regions that would expel the produced CH$_4$ under the permafrost and/or CH$_4$ hydrates into the water column and lead to rapid increase in the atmospheric CH$_4$ and trigger global warming. Increases in CH$_4$ levels in the ocean and in the atmosphere constitutes a positive feedback for global warming. However, it should be noted that biogeochemical cycles, characteristics of ocean water masses, frequencies and magnitudes of the occurrence of eddies would differ among the ocean areas depending on biological conditions, hydrographic conditions, and other environmental conditions.

6.3 Further understanding of CH$_4$

Further, I would examine the vertical profiles of CH$_4$ in the Southern Ocean where the vertical mixing helps to upwell the poor-CH$_4$ water in deeper water to the surface water. The relation between SR and AOU and other factors may impact CH$_4$ distribution in vertically need to examine. Consideration of the influence of the warm-core eddy on CH$_4$ distribution even though it accounts a small fraction of the total number of eddies (3%). From this study, it clearly shows that the effect of the warm-core directly contribute to the vertical distribution of dissolved CH$_4$ in the water column. Cold-core eddies occupy approximately 125 (or 97% of the total number of eddies) in the Arctic Ocean so that cold-core eddies would transport CH$_4$ like the warm-core eddies did. Further field observation of CH$_4$ crossing a cold-core eddy is a chance to understanding CH$_4$ distribution within and outside the water core. Furthermore, the effects of climate change impact physical, biogeochemical ocean characteristics as well as CH$_4$ distribution. Changing in CH$_4$ distributions and estimations need to do further research.
REFERENCES


