Spatial variability of methane abundance in a British Columbian fjord system

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Non technical summary

Methane is both a highly insulating greenhouse gas, which has therefore contributed to climate change past and present, and a source of organic carbon for many microbes in low-oxygen environments. For these reasons, improving our understanding of methane distributions in the ocean is crucial. While previous studies have identified some oceanographic and terrestrial sources of methane, the sizes of and periodic changes in methane concentrations are less understood. One important site of methane use and production by microbes is anoxic fjords. High methane concentrations associated with bacteria have been studied in the fjord of Saanich Inlet, Vancouver Island. In contrast, the Ocean 444 student study investigated the nearby Effingham Inlet, Vancouver Island, in an attempt to determine the distribution of methane in a complex, three-basin fjord system. When new water periodically replaces older, more anoxic water, methane concentrations are expected to decrease. I predicted the highest methane concentrations in the innermost, most isolated inlet, although less than in previous studies due to a speculated recent flushing of the basin. In order to undertake this study, water samples were collected at three stations in each basin of Effingham Inlet, aboard the *R/V Barkley Star*. The cruise took place from March 19-23 2010. At each station, water samples from several depths were collected and later equilibrated with nitrogen headspace. All samples were analyzed using a Gas Chromatograph-Flame Ionization Detector. Methane concentrations were indeed highest at the bottom of the inner basin, but were also high deep in the middle basin. Concentrations were much smaller in the outer basin, and near the surface. These results suggest that these basins have actually not been completely flushed recently, and that methane-using microbial communities may be similar to those found in other Vancouver Island fjord systems.

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Abstract

Methane abundance and distribution was studied in Effingham Inlet, British Columbia in order to determine the distribution of methane in complex, three-basin fjord system and compare different fjords in the same geographical area. I hypothesized highest methane concentrations in the innermost, most isolated inlet, although less than in previous studies due to a recent flushing of the basin. Improving our understanding of methane sources, sinks, and fluxes is crucial because methane is a highly insulating greenhouse gas and has therefore contributed to climate change past and present, and because many microbes either produce or oxidize methane through metabolism. In order to undertake this study, water samples were collected at three stations in each basin of Effingham Inlet, aboard the *R/V Barkley Star*. The cruise took place from March 19-23 2010. At each station, discrete water samples from several depths were collected and later equilibrated with nitrogen headspace. All samples were analyzed using a Gas Chromatograph-Flame Ionization Detector. Methane concentrations ranged between 0 and 100 nmol L^{-1} at each depth in the outermost basin and near the surface throughout the Inlet, but ranged between 1984 and 1423 nmol L^{-1} near the bottom of the inner basin and measured 1423 nmol L^{-1} in the depths of the middle basin. The lower surface values suggest that there is not a significant surface source from Effingham River. These results also suggest that these basins have not been fully recently oxygenated, and that the methane cycle in this fjord is similar to those in other Vancouver Island fjords.

Introduction

The global methane cycle is composed of several sources, both oceanographic and terrestrial. Previous studies have identified terrestrial sources such as tundra, wetlands, and agriculture/livestock, as well as oceanographic sources such as surface zooplankton, deep sea seeps and mud volcanoes, methane-producing bacteria, and methane hydrates. Although methane sources are identifiable, the relative magnitude and distribution of each source are unclear (Dlugokencky et al. 2009; Patra et al. 2009). Fung et al. (1991) acknowledged the difficulty of modeling future methane changes due to the lack of research. Although several studies have been completed since that publication, methane distribution and abundance are still poorly understood.

Further study of this gas is necessary because methane plays a significant role in climate change and marine organisms. As a greenhouse gas, methane is a much more powerful insulator than both carbon dioxide and water (Schmidt 2003). This hydrocarbon currently makes up a small portion of the total atmospheric greenhouse gas concentration, due to its relatively short residence time as it quickly oxidizes to carbon dioxide. Currently, ambient air typically has 1-2 ppm methane concentrations (Salmi 2009), which translates to 30-40 nmol L^{-1} in saturated seawater. However, its current residence time of ten years will increase if methane production increases, as it has done over the past few decades (Schmidt 2003). In the past, small temperature increases have led to the dramatic release of terrestrial methane in wetlands, which may be relevant to the current warming trend (Schmidt 2003). In anoxic or hypoxic regions, atmospheric increases in methane are expected to exacerbate preexisting oxygen minimum zones (Zaikova et al. 2009). In other words, oxygen minimum zones can serve as a negative feedback for increases in greenhouse gases.

These changes in methane are important not only in terms of climate change but because they affect microbial communities. While many oceanographic sources of methane are associated with hydrothermal systems or continental shelves, anoxic fjords are also important, especially as ecosystems for both methanogens and methylotrophs. Fjords are one type of estuary, and although shelves and estuaries make up only 15.4% of oceanic area, they are thought to be the source of 68.7% of all oceanic methane emissions (Abril et al. 2002). Methane-consuming bacteria, called methanogens, are chemolithoautotrophs that contribute to these emissions. They rely on methane as a carbon source. Bange (2006) simplifies this reaction as:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

This reaction is only favored in anoxic environments, which in the ocean tend to be either sediments or the digestive tracts of organisms (Reeburgh 2007). Conversely, a key sink for methane is methane-oxidizing bacteria called methylotrophs (Lilley et al. 1982). The reaction used by these bacteria is simplified as (Reeburgh 2007):

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Microbial communities in anoxic regions divert more energy from higher trophic levels than do other microbial communities, so methane changes in these areas affect not only bacteria but larger organisms too (Diaz and Rosenberg 2008).

Previous studies have both illuminated and complicated our understanding of the global methane cycle and the methane cycle around Vancouver Island. An early study identified the ocean as a net sink of atmospheric methane, and determined that most of this methane comes from wetlands and tundra (Fung et al. 1991). In contrast, other studies have focused on the ocean as a source of methane to the atmosphere. Marine geological sources of methane are widespread

at continental shelves and hydrothermal systems, and include mud volcanoes, seeps, and hydrates (Judd et al. 1997).

In contrast, methane has a biological source in many fjords worldwide. In the Baltic Sea, methane is highly variable, ranging from 4.5 – 120 nmol L^{-1} at the surface but reaching 2700 nmol L^{-1} at depth (Bange 2006). In one extreme case, methane concentrations have been measured at more than 30,000 nmol L^{-1} Marianger Fjord (Bange 2006). In the Mediterranean, estuarine methane concentrations ranged from 0 to 1263 nmol L^{-1}. Furthermore, concentrations in both regions have been found to be highly seasonal, reflecting the sensitivity to the availability of organic matter (Bange 2006).

Methane is also present in the water column in Saanich Inlet, British Columbia (Lilley et al. 1982). This Inlet is a 250 m deep fjord at the Southern End of Vancouver Island (Fig. 1). Methane concentrations are highest here at 30 m and at depth, reaching 1600 nmol L^{-1} at the bottom (Lilley et al. 1982). River input is thought to cause the shallower maximum. A more recent study found methane concentrations highest at depth in the winter, spring and summer, but only reaching 734 nmol L^{-1} (Zaikova et al. 2009). A smaller methane peak also appeared at the boundary between oxic and anoxic waters, around 100 m. During some years in the fall, deep water renewal can result in flushing of the basin, thereby increasing oxygen and reducing methane concentrations. The dense incoming water displaces the anoxic, less dense bottom water upward, causing mixing and disrupting the pattern of methane concentrations increasing towards the bottom. After a flushing event, methane concentrations linger below 30 nmol L^{-1} throughout the water column (Zaikova et al. 2009).

Fig. 1
Map of Vancouver Island, Canada and surroundings. Effingham Inlet's location is marked by a white star, Clayoquot's by a dotted star, and Saanich's by a striped star.

In Clayoquot Sound, also on Vancouver Island, British Columbia, sinking aggregates seem to be another source of methane flux (Fig. 1). Methanol in detrital matter reached 70,000 nmol L^{-1}, and 16s rRNA sequencing revealed a significant methylotrophic community. This study suggests that sinking particles may provide an important carbon source for methylotrophic bacteria in the water column in this environment (Miller 2010).

Although methane and methanol concentrations have been studied in Saanich Inlet and Clayoquot Sound, other fjord systems surrounding Vancouver Island are less well studied.

Effingham Inlet, in Barkley Sound on the West Coast of Vancouver Island, is one such system that is both similar to and more complex than Saanich and Clayoquot (Fig. 1). This Inlet is 17 km long and on average 1 km wide, with three distinct basins and two sills (Hay et al. 2008). Effingham River flows into the source of the Inlet. The inner, or northernmost, basin is almost always anoxic, while the middle is either anoxic or suboxic, and the outermost is oxic (Hay et al. 2008). The upper basin is not the deepest at 118 m depth, but the 40 m sill prevents some flushing events from penetrating that far into the Inlet (Hay et al. 2008). The middle basin, in contrast, is much deeper at 205 m but is flushed more frequently. The outermost basin is 90 m deep and is thought to circulate freely with the rest of Barkley Sound. The variable depths and proximity to Barkley Sound and the River of these three basins, as well as the lack of previous methane study here, mean that this location offers an opportunity to better understand marine methane distributions, both in terms of comparing the three basins to each other and comparing Effingham Inlet with other coastal fjords. Furthermore, a recent flushing event may have occurred in late 2009, and the effects on the water column had not been studied extensively (Keil, pers. comm.).

Due to the possible recent flushing event, as well as river input at the mouth of Effingham Inlet, I hypothesized that methane will be most prevalent in the innermost basin, at depth and near the surface, but that concentrations will be significantly lower than those found by Lilley or Zaikova. Furthermore, I hypothesized methane concentrations comparable to those in ambient air in the middle and outer basins because they are thought to flush more frequently.

Methods

To test these predictions, shipboard analysis was done at three stations in Effingham Inlet aboard the *R/V Barkley Star* from March 20-22 2010 (Table 1; Fig. 2). The sampling procedure roughly followed Eric Olson, pers. comm., and Lilley et al. (1982) (Fig. 3). Each station corresponded with one of the three basins in the Inlet.

Water samples were collected using four 10 L Niskin bottles. In order to determine how methane abundance varies throughout the water column, bottles were closed at 10 m, 50 m, 80 m, 10 m above the bottom, and just above the sea floor.Because dissolved gases are prone to air contamination, being the first to sample each Niskin was a priority. At most stations and depths, duplicates and triplicates were collected both to measure precision and in anticipation of analysis error. Water was collected from each Niskin in glass oxygen bottles with ground glass stoppers. Two types of bottles were used; some with wider bases that narrowed at the top with small stoppers and some more cylindrical bottles with much longer stoppers. Once filled until overflowing, samples were poisoned with 200 uL saturated mercuric chloride ($HgCl_2$) solution. Because each bottle contains fewer than 200 mL of water, this volume of $HgCl_2$ resulted in a greater than 1% solution, which is thought to be a sufficient concentration to halt biological activity that could alter methane concentrations (Stutsmann, pers. comm.). Next, bottles were

Table 1
Sampling Stations in Effingham Inlet, Vancouver Island.

Station	Location	Latitude	Longitude	Depth
EF1	Upper Effingham Inlet	49 04.32 N	125 09.45 W	115 m
EF2	Middle Effingham Inlet	49 02.54 N	125 09.14 W	200 m
EF3	Lower Effingham Inlet	49 00.67 N	125 10.23 W	80 m

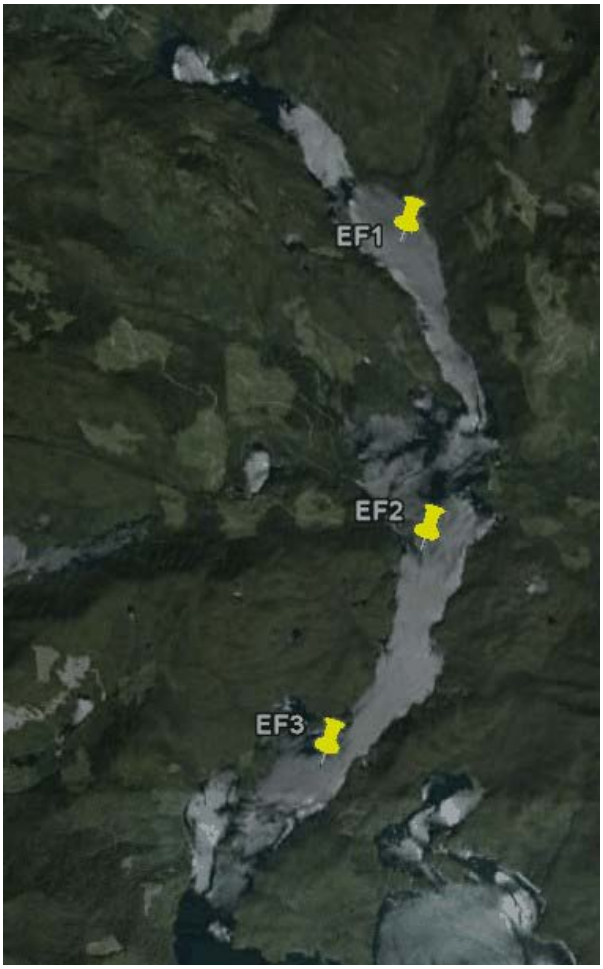

Fig. 2
Map of Effingham Inlet. Each labeled pushpin marks one of the three stations in Effingham Inlet, each in a different basin.

carefully sealed with glass stoppers to prevent the introduction of air bubbles. Because methane abundances are often expected to be at the lower end of the analyzing instrument's sensitivity, any air bubbles could skew the results drastically (Salmi 2009). For transportation back from the Bamfield Marine Sciences Centre to the University of Washington, bottles were wrapped with black electrical tape.

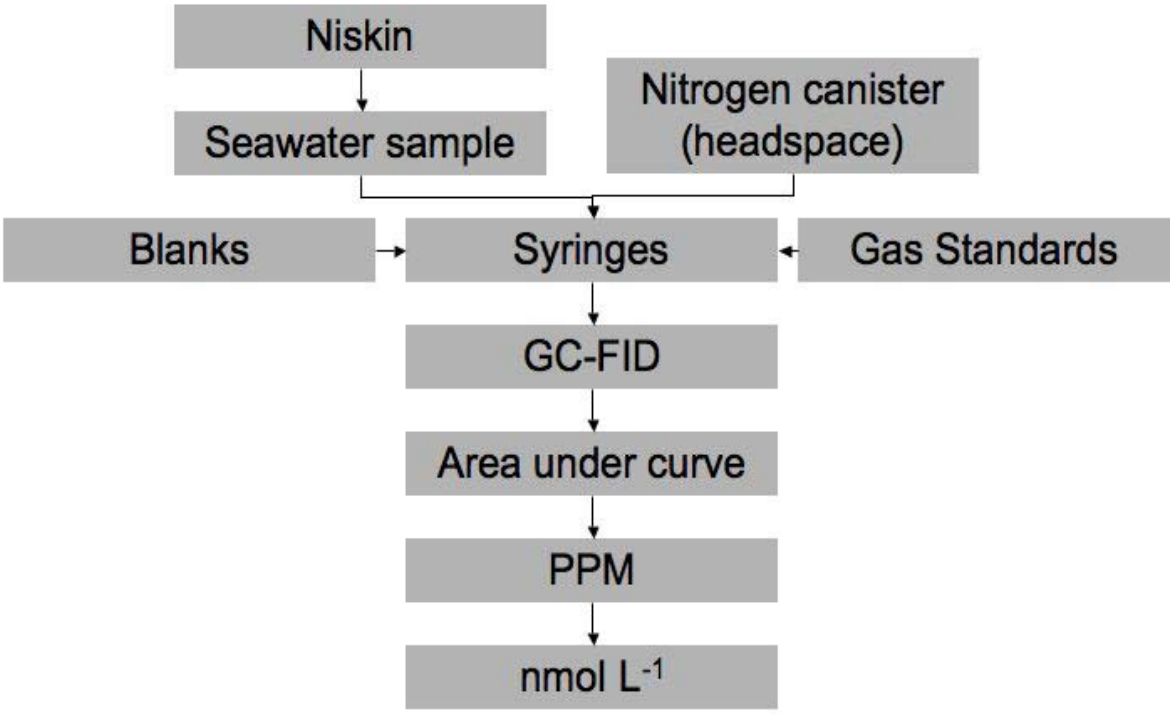

Fig. 3
A schematic diagram of the sampling method is shown, including shipboard sample collection, lab work, and calculations.

Lab analysis of samples was completed at the University of Washington using a Gas Chromatograph Flame Ionization Detector (GC-FID) equipped with an integrator to display the peaks. Samples were analyzed roughly a month after collection over a three day period. From each sample bottle, 40 mL of seawater was drawn into a 60 mL syringe equipped with a three-way valve and an 18 gauge needle. After switching to a 23.5 gauge needle that is less damaging to rubber septa, the syringe was connected to a nitrogen canister through a septum. After withdrawing 20 mL of nitrogen gas, the syringe was shaken vigorously for one minute to quicken equilibration. Next, 10 mL, or half, of the headspace was injected into the GC-FID so as

to flush the tubing. A dial on the GC-FID was then switched from ‘load’ to ‘inject’ and 2 mL of that injected headspace was analyzed. The integrator printed out a chromatogram for each run displaying the response time and the unitless area under each curve. Each syringe contained enough headspace for two injections and each sample bottle contained enough seawater for two draws. Therefore, there were four injections for each bottle of seawater, except for the few samples that were lost.

In addition to seawater samples from Effingham Inlet, several standards and blanks were also analyzed. Two types of blanks were run: both N_2 gas-filled syringes and syringes filled with 40 mL of deionized water and 20 mL of nitrogen gas. This dual approach could show whether either N_2 or water led to unexpected methane peaks. In order to calibrate the GC-FID, and to convert sample concentrations from area under a curve to ppm, each day a calibration line was made from two standard hydrocarbon mixtures with concentrations of 10 and 50 ppm.

Statistical analysis was also performed on all samples and standards. For both 10 ppm and 50 ppm standards, the mean areas under the curve were calculated, as well as the standard deviation. Precision was calculated in terms of standard deviation divided by the mean, as a percent. For samples, the mean ppm in the headspace was calculated for each depth at each station, as well as the standard deviation.

Additional mass balance calculations were performed to convert the headspace ppm values into molar concentrations in seawater. In order to calculate this concentration, 95% of the methane in the seawater was assumed to diffuse into the headspace (Lilley et al. 1993). Using the volume of the headspace and the seawater, and the STP volume of a gas:

$$[CH_4] = nmol\ L^{-1} = (ppmv\ CH_4)(1\ L\ CH_4/10^6\ L\ headspace/1\ ppmv\ CH_4)(1\ mol\ CH_4/22.4\ L\ CH_4)(10^9\ nmol/1\ mol)(L\ headspace/L\ seawater)(.95)$$

These concentrations were then plotted in Microsoft Excel as depth profiles.

Results

Sample Results

Methane concentrations were calculated at several depths at each station. Molar concentrations varied significantly both by station and by depth (Fig. 4). In the inner basin, EF1, methane ranged from 0-32 nmol L^{-1} above 50 m. However, concentrations increased by two orders of magnitude within 20 m of the bottom: 1984 nmol L^{-1} at 100 m before decreasing to 1423 nmol L^{-1} at 110 m. Additionally, the water samples collected from 100 m and 110 m at this station smelled strongly of methane, which corresponds with the higher measured concentrations.

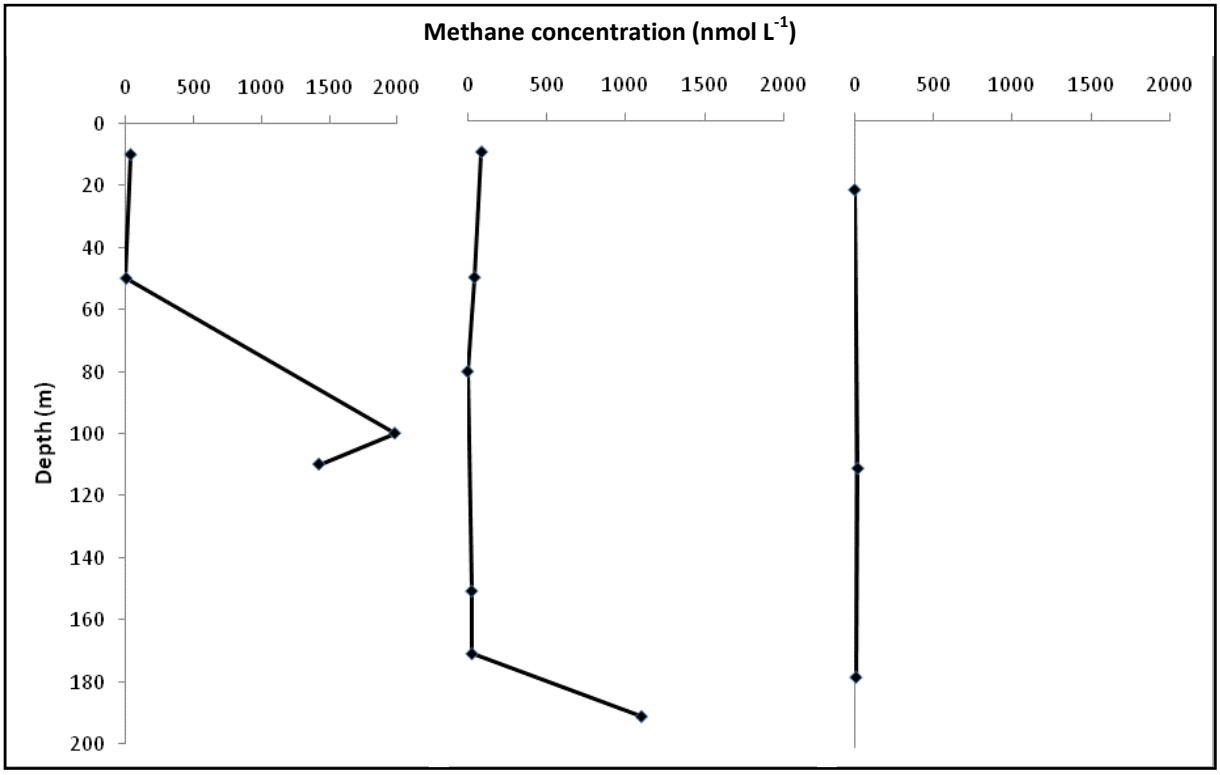

Fig. 4
Depth profiles for methane at each of the three stations in Effingham Inlet. Depth is on the y axis from 0 to 200 m while the x axis shows methane concentrations between 0 and 2000 nmol L^{-1}. From left to right: EF1 in the inner basin, EF2 in the middle basin, and EF3 in the outer basin. Concentrations range from 0 nmol L^{-1} to 1984 nmol L^{-1}.

At EF2, in the middle basin, methane varied between 0 and 88 nmol L^{-1} from 10 m to 150 m, but with no discernible pattern. As at EF1, methane concentrations then increased, here to 1096 nmol L^{-1}. Therefore, although this basin did display the same basic pattern of methane increasing at depth, there was not the same fine-scale pattern of a methane maximum at the second-to-deepest depth and a slight drop-off at the deepest depth. Furthermore, the highest concentration in the middle basin was roughly half of that in the upper basin. Unlike the upper two basins, the outermost basin had methane concentrations between 0 and 20 nmol L^{-1} at every depth sampled (10 m, 50 m, 80 m).

Statistical Analysis

Standard deviations for these water sample runs were calculated for each depth at each station. Values for standard deviation ranged between 2 and 74 nmol L^{-1}. There was no clear correlation between the magnitudes of standard deviation and mean methane concentration, which actually means that there was a correlation between methane concentration and standard deviation as a percent of the mean. In other words, at the deep depths in the inner basins, where methane was more abundant, the standard deviations were only 3-5% of the means, whereas in shallow or out areas with lower methane concentrations, the standard deviations were almost as large as the means (10-93%).

These concentrations were calculated based on data from the GC-FID integrator as well as calibration curves produced from gas standards. Standards at 10 ppm and 50 ppm were run several times per day, averaged, and plotted. In these plots, (0,0) was also assumed to be a point, because a curve with no area means that there are no parts per million (Holtgrieve, pers. comm.). Each day of lab work, these three-point calibration curves were linear, as expected, with R^2 values of 0.9996 and 0.9998. However, there was variation every day in the slope of the line. For example, between April 19 and April 21, the slope, and therefore the conversion factor between

area under the curve and ppm, shifted from 284950 to 261239. This 8% shift required modifying the conversion calculation every day. Furthermore, the location of the methane peak on the chromatogram drifted daily, measured as response time. The response time began at 0.46 on April 19, but ended at 0.32 by April 21. Despite this shift, the standard deviation for both 10 ppm and 50 ppm on any individual day was always small, ranging between 1.26 and 4.26 % of the mean.

In addition to standards, blanks were also run daily. Of 25 total blanks, 11 featured no discernible methane peak, and most showed no peaks at all. The remaining 14 had an average methane peak corresponding to 2.9 nmol L^{-1}. Overall, there was no consistently significant methane peak. In other words, because standard deviations for the samples ranged from 2 to 74 nmol L-1, 2.9 nmol L^{-1} is well within the standard deviations of most methane concentrations in this study.

The final type of sample run was room air. Unlike the blanks, these injections did consistently feature a methane peak. The average concentration in the headspace corresponded to 2.4 nmol L^{-1}. However, there was also a separate, equally consistent peak in these room air samples that occurred with almost no other samples: a strong peak at 0.27. The identity of this gas is unknown, but does not correspond to methane or water.

Discussion

As predicted, methane concentrations in many parts of Effingham Inlet exceed those concentrations found in the atmosphere. The only basin without significant methane abundance is the outermost basin, which can be attributed to the fact that this basin is the most exposed to the oxic waters of Barkley Sound. In addition to methane concentrations below 20 nmol L^{-1}, the outer basin's shallow depth, close proximity to Barkley Sound, and oxygen levels above 200

umol/kg (Emswiler and Linder, pers. comm.) all suggest that this basin has more in common with the rest of the Sound than the anoxic basins further down Effingham Inlet. For this reason, the remaining discussion will focus on the innermost basins.

The highest concentrations are at the bottom of the two innermost and isolated basins. While these abundances were smaller than the 2700 nmol L^{-1} measured in the anoxic Kiel Harbour in the Baltic Sea (Bange 2006), he highest value at EF1, in particular, exceeds those found by Lilley et al. (1982) in Saanich Inlet by almost 400 umol L^{-1}. In contrast, the highest methane concentration at EF2, 1096 nmol L^{-1}, and the value at 100 m at EF1, 1434 nmol L^{-1}, fall midway between Lilley et al.'s 1600 nmol L^{-1} and Zaikova's (2008) 734 nmol L^{-1}. Both previous studies, however, noted a mid-depth methane peak whereas this study did not. There are several potential explanations for this variation between studies, as well as the variation between the two basins.

Laboratory analysis error seems an unlikely explanation for this variation. Although the 10 ppm and 50 ppm standards produced different areas with different response times each day, the standard deviations for each individual day were less than 5% of the means, suggesting adequate precision on a short time scale. This precision is comparable to the 3% of Lilley et al. (1982). Almost half of blanks showed no methane peak, and the ones that did averaged only 2.9 nmol L^{-1}, which is at least one order of magnitude smaller than most of the methane concentrations throughout the water column, and all of the ones at depth. The methane peak in room air, averaging 2.4 nmol L^{-1}, has the same level of significance as that of the blanks. This room air peak is higher than, but comparable to the value of 1.8 nmol L^{-1} found by Salmi (2009). This study could have resulted in higher room air values because the syringes may have had lingering traces of methane-rich seawater, although they were rinsed with deionized water

between runs. However, the methane peak is not the only important peak for the room air samples. Because the consistent room air peak at 0.27 only appeared in two of the seawater sample injections, room air seems not have significantly contaminated the samples.

Compared with laboratory error, error in the field likely had more of an effect on the calculated methane concentrations. Air contamination likely lowers measured methane concentrations in most studies. However, the relatively slow sampling speed, and the several minutes that elapsed during triplicate sampling in this study may have a larger effect than in most other studies. The duplicates and triplicates were almost always collected by sampling multiple times from a single Niskin bottle. Furthermore, once the bottles were filled until overflowing, 30 seconds to one minute elapsed during mercuric chloride injection, during which time samples were directly exposed to the atmosphere. For these two reasons, the introduction of atmospheric air into the samples was likely, which would lead to erroneously low concentrations of methane. There are also some sample bottles that may not have received the full 2000 uL of mercuric chloride, if some spilled out of an already overflowing bottle. The mercuric chloride is meant to halt both methane-producing and methane-consuming microbial processes, so error in this step could lead to misleadingly high or low methane concentrations. These assumed sources of error render the lower methane concentrations at EF1 and EF2 unreliable, particularly the second and third draws. The most extreme example of this is at 10 m in EF1: methane concentration was 32 nmol L^{-1} while the standard deviation for this value is 30 nmol L^{-1}. In these shallow depths, therefore, the values are statistically significantly different from the 1000+ nmol L^{-1} concentrations at depth, but not from each other and not from the other shallow depths at different stations. Furthermore, the high concentrations at depth are statistically significantly different from one another.

This lack of a clear pattern at shallower depths is an important difference between this study and the previous studies in Saanich Inlet. The cause may geographic. Saanich Inlet is close to the Frasier River, which is a large source of freshwater input from Vancouver Island [Lilley et al. 1982]. Although the methane concentrations of the Frasier River were unknown, similar river systems have seen methane concentrations in excess of 500 nmol L^{-1}, making the Frasier a potential methane source near the surface (Lilley et al. 1982). In contrast, Effingham River is a comparatively small freshwater source (Hay et al. 2009). Salinity data support this idea: Lilley et al. (1982) found salinities below 30 down to 70 m, whereas this study saw salinities below 30 only a few meters below the surface, and only at 3 m in the innermost basin (Linder, pers. comm.). Although some salinity difference could be attributed to recent rainfall or evaporation, the extent of the difference suggests that the lack of a freshwater methane source caused the lack of a shallow methane peak. In the global context, the 4 to 100 nmol L^{-1} surface concentrations in Effingham Inlet compare well with the 4.5 to 120 nmol L^{-1} measured in the an estuary in the Baltic Sea (Bange 2006), which also did not have a notable freshwater source (Bange 2006).

While freshwater input variation may explain the variation between studies at the surface, lack of sampling resolution may explain the differences at mid-depth. Zaikova et al. (2009) found both methane concentration and oxidation peaks at 100 m, which was also the boundary between hypoxic and oxic waters. Around this depth, single carbon-metabolizing bacteria species were detected. In contrast, this study found no such methane peak at the hypoxic boundary layer, which seems to be around 55 m in the inner basin and 85 m in the middle basin (Emswiler, pers. comm.). However, the lack of a clear peak in this study may be due to lack of resolution; Zaikova et al. (2009) collected samples at many more depths. In this study, no depths were sampled between 50 and 100 m in the inner basin, so any peak around 55 m would be

missed. Similarly, the lack of depths sampled in the middle basin could mean a mid-depth peak was overlooked.

While freshwater input and sampling resolution seem likely contributors to variation at the surface and mid-depths, temporal differences may explain the methane concentrations at depth, and why they differ from those found in Saanich Inlet. The differences are of two kinds: higher overall concentrations in Effingham Inlet, and the spike in methane at the second-to-deepest depth in the inner basin. Because periodic flushing events are thought to decrease methane concentrations drastically, the high concentrations suggest that the inner two basins have not been flushed recently. This result agrees with data suggesting there has been no complete flushing since at least March 2009 (Linder, pers. comm.). Alternatively, there could be another environmental factor that helps methane-producing methanogens thrive in these basins. However, the dramatic decrease in methane concentrations in Saanich Inlet after one flushing event, from 700+ nmol L^{-1} to about 30 nmol L^{-1} suggest that flushing is indeed the dominant sink for methane in these environments.

And yet, while the basins do not seem to have been completely flushed recently, there are still two pieces of evidence that a partial flush has occurred. First, concentrations in the middle basin are significantly lower than those in the inner basin, despite the deeper depth in the middle basin. The middle basin is more vulnerable to dense bottom water input both because of a deeper sill and closer proximity to Barkley Sound. Therefore, oxygenated bottom water may have poured over the sill into the middle basin to a greater extent than the inner basin. Second, the decrease in methane in the inner basin between 100 m and 110 m suggests a partial flushing of oxygenated water. With no deep water input, methane concentrations would be expected to increase down to the sediments, where methane concentrations can reach as high as 3000 nmol

L-1 in Saanich Inlet (Devol 1983). However, an actual decrease in methane concentration near the bottom may be from a recent input of oxygenated bottom water. Ten meters above this local minimum, however, at 100 m, the methane concentration is higher, which suggests that the basin has not been completely renewed with oxygenated water. The anoxia in both basins supports this idea (Emswiler, pers. comm.).

Conclusion

Methane concentrations in Effingham Inlet were found to vary significantly between stations, depths, and in comparison with studies in Saanich Inlet. Surface concentrations were consistently lower than 100 nmol L^{-1}. However, there was no discernible pattern at these depths, and the high standard deviations, likely caused by error in the field and the lower limits of the GC-FID's sampling sensitivity, render these measurements problematic. Nevertheless, these sites of low methane abundance are statistically differentiable from the much higher concentrations at depth in the innermost basins. In the inner basin, methane spiked to 1984 nmol L^{-1} at 100 m before decreasing again to 1423 nmol L^{-1} at 110 m. In the middle basin, methane increased dramatically to 1096 nmol L^{-1} at 190 m, close to the bottom.

The lack of a surface or mid-depth peak in Effingham Inlet, as opposed to Saanich Inlet, is likely due to decreased freshwater input and fewer depths sampled, respectively. The higher overall concentrations, coupled with the actual decrease of methane at the bottom of the inner basin, suggest that while these two basins have not been completely flushed recently, a recent pulse of dense, methane-depleted water is likely.

There are numerous opportunities for future study of methane in Effingham Inlet. More depths must be sampled, particularly below 50 m, in order to confidently determine whether a peak exists at the hypoxia boundary, and whether there is evidence of a recent flushing event in

the middle basin. Furthermore, methane concentrations alone do not reveal the actual source of this methane, nor the relative importance of atmospheric emission, oxidation, and flushing as sinks. Furthermore, more study is needed to determine the extent to which the methane is part of a microbial community, and whether these bacteria are mostly methylotrophs, as in Clayoquot Sound, or methanogens. In addition to sampling for these bacteria, sampling for methanol and sulfur compounds are also important factors in determining the relationship between methane and microbes in this environment. Finally, because seasonal variability has greatly affected abundance in the Baltic and Mediterranean (Bange 2006), as well as other regions (Reeburgh 2007), studying the temporal variability at Effingham Inlet is also important.

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