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On the distribution of dissolved methane in Davis Strait, North Atlantic Ocean

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ABSTRACT

Depth profiles of dissolved methane were measured along three transects of Davis Strait and the northern Labrador Sea in October 2011. Concentrations ranged from 0.2 nmol L^{-1} (6% saturation) in the remarkably methane depleted Baffin Bay Deep Water to 38.8 nmol L^{-1} (1057% saturation) in localised subsurface anomalies near the Baffin Island Shelf. These anomalies may be the result of natural gas seepage and this hypothesis is supported by the distribution of potential sea surface oil slicks detected by satellite radar backscatter. In contrast, methane concentrations within the Baffin Island Current 200 km to the south of these anomalies were only slightly above atmospheric equilibrium. Methane was moderately supersaturated in West Greenland Shelf Water (<200%) with a distribution consistent with a sediment source. These measurements represent the first detailed baseline study of the vertical distribution of dissolved methane in an important Canadian Arctic Archipelago outflow region.

1. Introduction

The Arctic is identified as being particularly sensitive to radiative warming with the loss of sea ice occurring at a seemingly unprecedented rate (Kinnard et al., 2011). There has been speculation that reserves of methane hydrate stored in Arctic shelf sediments and permafrost may be destabilised over a relatively short time scale by climate warming, with the result that huge quantities of the greenhouse gas methane (CH_4) are released to the water column and hence the atmosphere (Kennett et al., 2002; Schaefer et al., 2011). In addition to the potential contribution to radiative climate forcing, large scale methane release from Arctic sediments could contribute to ocean acidification and regional oxygen depletion through the microbial oxidation of dissolved CH_4 to carbon dioxide (Boetius and Wenzhöfer, 2013). The process of hydrate erosion may already be underway in shallow Siberian Shelf waters (Shakhova and Semiletov, 2007; Shakhova et al., 2010) and along the West Spitsbergen continental margin where numerous bubble plumes have been observed (Westbrook et al., 2009). In Canadian waters, Majorowicz and Osadetz (2001) estimated that the potential volume of gas stored in hydrates is 0.19–6.2 $\times 10^{14}$ m^3 in the Canadian Arctic Archipelago and 1.9–7.8 $\times 10^{13}$ m^3 on the Canadian Atlantic Margin. Very few studies of dissolved methane have been made in the eastern Canadian Arctic and most published data are for surface waters (e.g. Kitidis et al., 2010). Investigators face the challenge of distinguishing natural post glacial variability in Arctic methane fluxes from changes due to anthropogenic climate change without the benefit of long term observations. Hence there is a need for more detailed study of dissolved methane in Canadian Arctic waters in order to establish a baseline against which future changes, including the effects of hydrate decomposition, can be gauged.

This study presents 470 measurements of dissolved CH_4 made during three transects of Davis Strait between Greenland and Baffin Island by the R.V. Knorr in October 2011. The objectives of this work were to map the distribution of dissolved methane in order to identify sources and sinks in this region and to provide a high spatial resolution baseline study of high latitude methane dynamics.

1.1. Study area

Davis Strait is an important corridor for Arctic Water (AW) from the Canadian Arctic Archipelago flowing south through Baffin Bay to the North Atlantic Ocean. This cold, fresh, Baffin Island Current ($\theta \leq 1$ °C, $S \leq 33.7$) is largely confined to the upper 300 m of the water column along the Canadian continental margin. In contrast, the West Greenland Shelf/Slope is dominated by the northward-flowing warm West Greenland Shelf Water ($\theta < 7$ °C, $S \leq 34.1$) and West Greenland Irminger Water ($\theta > 2$ °C, $S > 34.1$) (after Curry et al., 2011). The Davis Strait bathymetry takes the form of a sill with a mean depth around 600 m that restricts deep water exchange between the ocean basins of Baffin Bay and the Labrador Sea (Tang et al. 2004). Three principal

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subsurface water masses have been indentified in Baffin Bay: Baffin Bay Intermediate Water (300–800 m), Baffin Bay Deep Water (800–1200 m), and Baffin Bay Bottom Water (>1200 m). To the south of Davis Strait, Labrador Sea Water is found from the surface down to around 2200 m depth.

Samples for dissolved methane were collected and analysed during three transects of Davis Strait shown in Fig. 1: the Northern Line (NL) which crossed southern Baffin Bay with 15 sampling stations; the Mooring Line (ML) with 18 stations mainly along the line of the sill; and the combined Northern Labrador Sea East (NLSE) and Northern Labrador Sea West (NLSW) sections with a total of 17 stations.

2. Methods

Seawater samples were collected using a rosette of 10 L Niskin bottles. Samples were then drawn into 160 mL volume borosilicate glass serum bottles (Wheaton Scientific, Millville, New Jersey), without the inclusion of bubbles, using a 30 cm length of flexible tubing and allowing each sample bottle to overflow by a minimum of two volumes. The samples were then immediately stabilised against further microbial activity by the addition of 50 μL of saturated of mercuric chloride solution, crimp-sealed with Teflon-faced butyl rubber septa, then stored at 4 °C prior to analysis, usually within 12 h.

Concentrations of dissolved methane were determined by a batch static headspace equilibrium/gas chromatography method after Neill et al. (1997). In brief, batches of sample bottles were thermally equilibrated to 22 °C in a water bath whereupon a 10 mL headspace of ultra-high-purity nitrogen was introduced into each bottle and the samples were shaken vigorously for 10 min to achieve phase equilibration. Aliquots of headspace gas were transferred by displacement through a short drying tube packed with magnesium perchlorate to the sample loop of a gas chromatograph (SRI Instruments, California, USA) equipped with a flame ionisation detector. Methane was separated on a 0.5 m pre-column packed with 80/100 mesh Porasil A and a 2 m main column packed with 80/100 mesh HayeSep A. The columns were held at 50 °C and configured to backflush the pre-column to vent once the methane analyte peak had reached the detector. Each sample run was referenced to automated 1 mL injections of 2.044 ppmv (parts per million by volume) and 8.181 ppmv CH_4 primary standards (Air Liquide). Additional measurements of a 101.62 ppmv CH_4 primary standard were used to construct calibration curves bracketing the full range of sample headspace mixing ratios encountered. Methane concentrations in the water phase were calculated using the Bunsen solubility coefficients of Wiesenburg and Guinasso (1979). The analytical precision of repeated injections of standard gas was better than 0.5% standard error, while the overall analytical precision, determined from measurements of triplicate samples drawn from selected depths, was around 2%. Air samples for methane analysis were collected daily from the upwind side of the ship in a glass syringe equipped with a 3-way stopcock and analysed in the same manner as the headspace samples. Temperature and salinity profiles were measured using Seabird SBE3T and SBE4C sensors while dissolved oxygen concentrations were measured with a pair of Seabird SBE43 oxygen sensors mounted on the CTD. These sensors are routinely calibrated and maintained by the Woods Hole Oceanographic Institute Calibration Laboratory, however, the oxygen sensor data should be interpreted with caution, as no Winkler titration measurements were available for calibration.

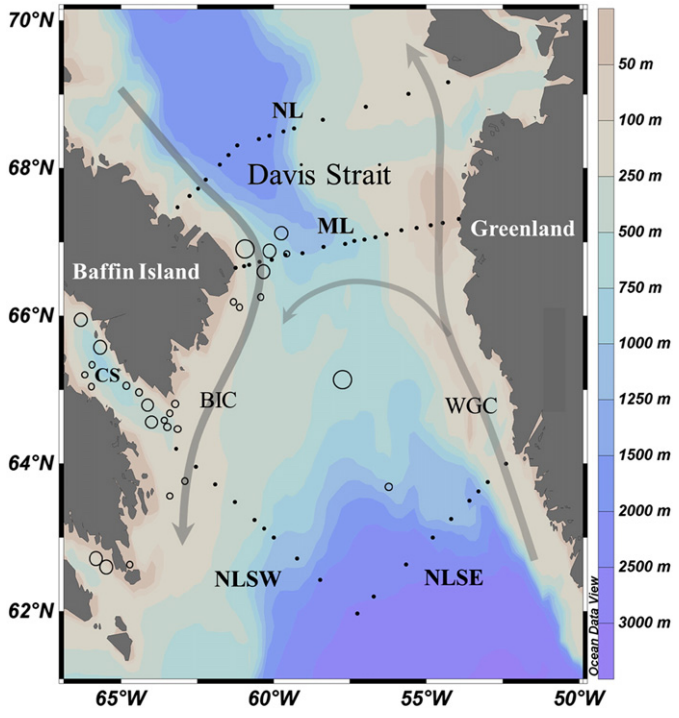

Fig. 1. The study area showing station positions (black dots) along the three transects: Northern Line (NL), Mooring Line (ML) and the Northern Labrador Sea East and West Lines (NLSE, NLSW). The general surface circulation is shown by arrows representing the Baffin Island Current (BIC) and the West Greenland Current (WGC), CS is Cumberland Sound. Open circles represent dark radar backscatter features identified on RADARSAT-images, potentially surface oil slicks (from Budkewitsch et al. 2013). Note that the satellite coverage does not extend as far north as the Northern Line.

3. Results and discussion

3.1. Air and surface water CH_4

A total of 23 air samples drawn over the study area returned a mean CH_4 mixing ratio of 1.80 ppmv (range: 1.78–1.84) and this figure, together with in situ temperature and salinity data, was used to calculate dissolved CH_4 saturation for the seawater samples. Plots of surface (<5 m) methane saturation along the NL, ML and NLS cruise tracks are shown in Fig. 2. Mean CH_4 surface concentration for the entire study area was 3.79 nmol L^{-1} (112% saturation) with a range of 2.82–5.58 nmol L^{-1} (89–174% saturation). For the central NL, CH_4 was mostly very close to atmospheric equilibrium, rising to modest supersaturations at the inshore stations. In the case of the ML and NLSW/NLSE, elevated levels of CH_4 were most prominent near the Greenland Shelf. A notable exception was at the most inshore ML station where surface CH_4 saturation was only 89%. Methane undersaturation in high-latitude surface water has been attributed to seasonal ice melt (Kitidis et al., 2010) but in this case the shallow water column was relatively well mixed ($\delta S/\delta z < 0.001$) and salinity cannot account for the change between undersaturation in the near surface water to supersaturation in the bottom water (see following section) even if dissolved methane was entirely absent in the glacial meltwater input. Although no sea ice was observed during this study, the influence of glacial melt water on regional dissolved methane distributions cannot be ruled out. Indeed, glacial melt water is the predominant source of fresh water to the eastern Davis Strait (Azetsu-Scott et al., 2012).

3.2. Sea/air CH_4 fluxes

The flux F of CH_4 across the air/sea interface was calculated for each station using the equation

$$F = k_w(C_w - C_a)$$

where k_w is the gas transfer velocity for methane, C_w is the measured methane concentration in the surface water and C_a is the equilibrium concentration of methane at surface water temperature and salinity calculated using the measured CH_4 atmospheric mixing ratio and the Bunsen solubility coefficient of Wiesenburg and Guinasso (1979).