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Factors controlling methane and nitrous-oxide variability in the southern British Columbia coastal upwelling system



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ABSTRACT

Coastal upwelling systems are important marine sources of methane (CH₄) and nitrous-oxide (N₂O). Current understanding of the controls on CH₄ and N₂O distributions in these coastal waters is restricted by limited data availability. We present the first multi-year measurements of CH₄ and N₂O distributions from the seasonally upwelling shelf waters of British Columbia, Canada, a coastal end-member of the north Pacific oxygen minimum zone (OMZ). Our data show significant seasonal differences in CH_4 and N_2O distributions and fluxes driven predominantly by upwelling. Methane is supplied to the water column primarily from sediments (especially near methane seeps), and is transported to the surface mixed layer by upwelling. A positive correlation between CH₄ concentrations and salinity indicates limited inputs from Fraser River estuary waters to the study site. Shelf waters receive N₂O from a deep, off-shelf N₂O maximum in the OMZ core, and from nitrification in the water column and possibly sediments. Both the physical transport of N₂O and its apparent in situ production are enhanced under upwelling conditions. N₂O yields from nitrification, estimated from changes in N₂O and nitrate + nitrite $(NO_3^- + NO_2^-)$ along isopycnals, ranged from 0.04–0.49%, with the highest values observed under low ambient O₂ concentrations. Sea-air fluxes ranged from $-4.5-21.9 \,\mu$ mol m⁻² day⁻¹ for N₂O and 2.5–34.1 μ mol m⁻² day⁻¹ for CH₄, with the highest surface fluxes observed following summer upwelling over the broad continental shelf of southern Vancouver Island. Our results provide new insight into the factors driving spatial and inter-annual variability in marine CH₄ and N₂O in high productivity coastal upwelling regions. Continued time-series measurements will be invaluable in understanding the longer-term impacts of climate-driven variability on marine biogeochemical cycles in these dynamic near-shore waters.

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1. Introduction

Methane (CH₄) and nitrous-oxide (N₂O) are the most important greenhouse gases after carbon-dioxide and water-vapor, accounting for ~17% and 6% of the global radiative forcing of all greenhouse gases, respectively (IPCC, 2013). These gases are actively cycled in low oxygen sub-surface ocean waters and sediments, where intensive microbial activity drives a diverse suite of metabolic pathways.

The major processes driving marine N₂O cycling are nitrification and denitrification. N₂O is produced as a by-product of nitrification (stepwise oxidation of ammonium (NH₄⁺) to nitrite (NO₂⁻) and nitrate (NO₃⁻)), which is carried out by a variety of chemo-autotrophic bacteria and archaea under oxic to nearly anoxic conditions (Casciotti and Buchwald, 2012; Freing et al., 2012). N₂O yields from marine nitrification (i.e. mol N₂O produced per mol NO₂⁻ + NO₃⁻ produced) are highly variable, ranging from 0.004–0.4% (De Wilde and De Bie, 2000; Frame

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and Casciotti, 2010; Goreau et al., 1980; Punshon and Moore, 2004; Santoro et al., 2011; Stieglmeier et al., 2014), and have been shown to increase under low oxygen conditions (Frame and Casciotti, 2010; Goreau et al., 1980; Stieglmeier et al., 2014). The change in N₂O yield may be due to the tendency of nitrifiers to preferentially reduce $NO_2^$ to N₂O (nitrifier-denitrification) under O₂-limitation (Frame and Casciotti, 2010). Denitrification (the step-wise reduction of NO₃ to N₂ via NO_2^- , nitric oxide (NO) and N_2O) is typically confined to waters with $<5 \mu$ M O₂ (Codispoti et al., 2001), and is ultimately a sink of N₂O under anoxic conditions. However, the enzyme N₂O-reductase is more O₂-sensitive than the other N-reductase enzymes in denitrification, resulting in N₂O accumulation by partial/incomplete denitrification under very low (sub-micromolar) O₂ concentrations (Betlach and Tiedje, 1981; Dalsgaard et al., 2014). Indeed, denitrification appears to be a dominant source of N₂O in suboxic marine waters such as the Arabian Sea and West-Indian continental shelf (Bange et al., 2001; Codispoti et al., 2001; Jayakumar et al., 2009; Naqvi et al., 2000), and at the peripheries of OMZs (Bange, 2008; Castro-González and Farías, 2004). The highest N₂O production rates thus occur in low oxygen waters, where high N₂O-yields from nitrification co-occur with net-N₂O production from denitrification. Recent evidence suggests that N₂O



Abbreviations: WCVI, west coast of Vancouver Island; OMZ, oxygen minimum zone. * Corresponding author at: Dept. of Earth, Ocean, and Atmospheric Sciences, University

may be produced during dissimilatory reduction of nitrate to ammonium (Welsh et al., 2001), but this process appears to be confined to anoxic or very low O_2 (<10 μ M) waters (Lam et al., 2009).

Oxygen levels also exert a significant control on the marine CH₄ cycle. Until relatively recently, this gas was thought to be produced exclusively under anaerobic conditions during the biological or thermogenic breakdown of organic matter. Anaerobic CH₄-producing environments are generally confined to organic-matter rich sediments or within the earth's crust, although they can also be present inside sinking particles or digestive tracts of marine organisms (De Angelis and Lee, 1994; Holmes et al., 2000; Oremland, 1979; Sansone et al., 2001). Sediment-derived CH₄ is often mostly consumed by methanotrophic organisms, thus limiting CH₄ fluxes to the atmosphere, although the abundance of methanotrophs and their ability to consume CH₄ from sediments can be highly variable (Reeburgh, 2007; Steinle et al., 2015). Methane from subsurface organic deposits may migrate upward through coarse grained sediments or tectonic faults and escape the water column in seep-derived bubbles, which can enhance CH₄ transport into the mixed layer (Reeburgh, 2007; Riedel et al., 2002, 2009; Solomon et al., 2009). The release of CH₄ from these seeps shows strong spatial and temporal variability over a range of time-scales (from hours to years; Boles et al., 2001; Leifer and Boles, 2005; Tryon et al., 1999), and represents a potentially underestimated source of atmospheric CH₄. Moreover, the potential destabilization of CH₄-rich clathrate deposits under various ocean warming scenarios has prompted significant research effort in recent years (Archer, 2007; Solomon et al., 2009; Sowers, 2006). There has also been increased interest in other in situ sources of CH₄ in oxygenated marine surface waters, including the cleavage of methyl-groups from larger molecules, such as methylated sulfides (Damm et al., 2010; Florez-Leiva et al., 2013) and methylphosphonate (Metcalf et al., 2012; Karl et al., 2008). Due to their proximity to the ocean-atmospheric interface, these surface water pathways of CH₄ production may be important controls on seaair CH₄ fluxes.

Coastal upwelling regions are sites of active CH₄ and N₂O cycling, and disproportional contributors to the global marine emissions of these gases to the atmosphere (Bange, 2008; Nevison et al., 2004; Rehder et al., 2002; Sansone et al., 2001). High CH₄ and N₂O fluxes have previously been demonstrated in a number of upwelling regions (Bange et al., 1996; Bange et al., 1994; Pierotti and Rasmussen, 1980; Sansone et al., 2001), and recent research efforts have explicitly examined the effects of upwelling on coastal CH₄ and N₂O distributions in the waters of coastal Peru (Kock et al., 2015), Chile (Cornejo and Farías, 2012; Farías et al., 2015), Mauritania in NW Africa (Kock et al., 2008; Wittke et al., 2010), California (Cynar and Yayanos, 1992; Lueker et al., 2003; Nevison et al., 2004), Oregon (Rehder et al., 2002), and the Arabian Sea (Bange et al., 2001). In these upwelling systems, high surface productivity results in significant fluxes of organic carbon to sub-surface waters, fueling microbial O2-demand and driving redox gradients that favor N₂O and CH₄ production at relatively shallow depths (Naqvi et al., 2010; Sansone et al., 2001). Upwelling can also act to transport CH₄ and N₂O-rich sub-surface water into the mixed layer (Bange et al., 2001; Cornejo and Farías, 2012; Lueker et al., 2003; Naqvi et al., 2010; Nevison et al., 2004; Rehder et al., 2002). Short-term variability in upwelling over periods of hours to months has been shown to influence CH₄ and N₂O fluxes from coastal upwelling systems (Bange et al., 2001; Cornejo and Farías, 2012; Lueker et al., 2003; Rehder et al., 2002; Wittke et al., 2010). Upwelling of O₂depleted water has been linked to high N₂O production rates and seaair fluxes in a number of coastal systems, including the equatorial Pacific upwelling zone of Chile and Peru (Cornejo and Farías, 2012; Farías et al., 2009), and the Arabian Sea (Bange et al., 2001). The ongoing expansion and intensification of OMZs (Falkowski et al., 2011; Keeling et al., 2010; Stramma et al., 2010; Whitney et al., 2007) and the intensification of coastal upwelling due to stronger land-sea atmospheric pressure gradients (Bakun, 1990; Bylhouwer et al., 2013; Wang et al., 2015) - both of which are predicted effects of climate change – may thus lead to increased CH₄ and N₂O fluxes from coastal upwelling systems (Codispoti, 2010; Codispoti et al., 2001; Naqvi et al., 2010; Rehder et al., 2002). In addition to upwelling, other factors including eutrophication, sedimentary diffusion, freshwater inputs, and local bathymetry also appear to influence coastal N₂O and CH₄ distributions, resulting in high spatial and temporal variability in surface water concentrations and sea–air fluxes. This variability, combined with a scarcity of data, limits our ability to quantify CH₄ and N₂O emissions in coastal upwelling systems, and our understanding of longer-term (e.g. inter-annual) responses to environmental forcing.

In this article, we present new field data documenting the seasonal and inter-annual variability in CH4 and N2O concentrations and sea-air fluxes along the west coast of Vancouver Island (WCVI), British Columbia (BC). This coastal region is characterized by high seasonal productivity, resulting from wind-driven summer time upwelling. Our study site lies in close proximity to the large oxygen-minimum zone (OMZ) of the subarctic North Pacific, which supplies O₂-depleted water to the shelf during upwelling (Crawford and Peña, 2013). The persistently low O₂ levels in these waters have been declining in recent decades (Crawford and Peña, 2013; Whitney et al., 2007), and this has increased the likelihood of periodic upwelling of hypoxic water onto the shelf (Roegner et al., 2011), potentially enhancing the sea-air flux of CH₄ and N₂O. Our study site also contains a number of sedimentary bubble plumes (seeps), which have been identified as important sources of CH₄ to the water column along the Oregon Coast (Grant and Whiticar, 2002; Heeschen et al., 2005; Suess et al., 1999). The combination of upwelling, intensifying shelf hypoxia, and presence of seeps make the WCVI a potentially significant site for CH₄ and N₂O production and high sea-air fluxes. To date, CH₄ and N₂O distributions in this region have not been examined systematically.

Based on data obtained from five spring and summer cruises, we present detailed observations of the spatial and temporal variability of N_2O and CH_4 concentrations and sea–air fluxes, and use these observations to examine the processes affecting the distributions of these gases in the water column. In particular, we examine the influence of upwelling and fresh water (Fraser River) fluxes on CH_4 and N_2O distributions along the BC continental shelf, the potential contribution of sedimentary bubble-plumes to water column CH_4 budgets, and the oxygen-dependent changes in the N_2O yields from nitrification. This work represents a starting point for future time-series observations of CH_4 and N_2O dynamics in coastal BC waters.

2. Methods

2.1. Study site

The WCVI region is located at the northern end of the eastern, North Pacific upwelling region (Fig. 1). The upwelling season typically runs from June to September each year, while downwelling occurs between October and May (Bylhouwer et al., 2013). The onset, duration and intensity of upwelling are variable on an inter-annual basis, and this variability has been associated with the Pacific Decadal Oscillation (PDO) and El-Niño Southern Oscillation (ENSO) (Bylhouwer et al., 2013). There is a permanent oxygen minimum zone (OMZ; defined as O_2 concentrations less than 20 μ M) located between 800 and 1200 m depth in the water directly adjacent to the continental shelf (Fig. 1, inset). The study area is influenced by several local water masses. The Vancouver Island Coastal Current (VICC) is a buoyancy-driven freshwater current that runs in a northerly direction along the coast of Vancouver Island (shore-ward of the 150 m depth contour), fed by the Fraser river freshet (i.e. snow-melt runoff) during the spring and summer, and by coastal mountain rain runoff from Vancouver Island during the fall and winter (Foreman, 2000; Masson and Cummins, 1999). The VICC can extend to the bottom of the water column (Masson and Cummins, 1999). Over the outer continental shelf region, surface

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