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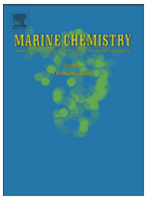

Impact of deep-water renewal events on fixed nitrogen loss from seasonally-anoxic Saanich Inlet

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ABSTRACT

We interpreted profiles of N_2/Ar ratios, δ^{15}N–N_2, and O_2 concentration collected in Saanich Inlet, British Columbia, Canada over an annual cycle. Our measurements and data from a regional cabled observatory indicated that four deep- or bottom-water renewal events occurred over our study period. Each event was correlated with a period of weak tidal currents, such that very low tidal mixing allowed inflowing water to retain its high density as it moved across the sill and into the deeper basin. By quantifying the concentration of excess N_2 in each month and the vertical diffusion rate, we determined that the N_2 production rate ranged from 1.7 ± 0.3 mmol N_2 m^{-2} d^{-1} in summer to 8.1 ± 2.8 mmol N_2 m^{-2} d^{-1} in winter. This depth-integrated estimate accounts for all pathways resulting in fixed (bioavailable) nitrogen loss as N_2 gas, including denitrification and anammox, and incorporates any benthic production of N_2 that diffuses into the overlying water column. In spring and summer, the maximum N_2 excess corresponded to the maximum δ^{15}N–N_2, indicating that denitrification approached completion. In these months, the average isotopic composition of the fixed N consumed was 7.5 ± 1.2‰. Following bottom-water renewal in fall, which brought in nutrient-rich, low-N_2 water, the N_2 concentration increased and became progressively more enriched in ^{15}N. The high rates of N_2 production in Saanich Inlet likely exist in other anoxic basins that undergo periodic deep-water renewal by nitrate-rich waters.

1. Introduction

We present a one-year time series of dissolved oxygen (O_2) concentrations, nitrogen/argon (N_2/Ar) ratios, and isotopic composition of N_2 in Saanich Inlet, British Columbia, Canada. We use these observations to estimate the loss of nutrients from the system by denitrification and related processes. We combine our measurements with data from a regional cabled sea-floor observatory to determine the timing of deep-water renewal and the mechanism for these events. Although this inlet is a small basin of limited global importance by itself, it serves as a model system for fjords with restricted circulation, common in similar geologic settings around the world.

Saanich Inlet, on southeastern Vancouver Island, transitions from sulfidic to oxic deep waters nearly every year and is one of the best-studied anoxic fjords in the world (Tunnicliffe et al., 2003). A 75-m depth sill at the northern end of the inlet restricts exchange into the basin, which reaches a maximum depth of 225 m (Fig. 1). High rates of surface productivity lead to high rates of aerobic respiration, consuming O_2 in the normally stagnant deep waters (Timothy and Soon, 2001; Gargett et al., 2003). Once O_2 is depleted, bacteria utilize other oxidants such as NO_3^- and SO_4^{2-} to decompose organic matter, typically resulting in complete consumption of NO_3^- and the production of H_2S in the bottom waters by summer (Anderson and Devol, 1973; Emerson et al., 1979). The anoxic basin is usually reoxygenated in early fall when upwelling off the coast of Vancouver Island causes dense water to form outside Saanich Inlet and flow across the sill into the basin (Anderson and Devol, 1973).

In oxygen-deficient environments, microbially-mediated reactions consume bioavailable inorganic nitrogen (fixed N), including nitrate, nitrite, and ammonium (NO_3^-, NO_2^-, and NH_4^+). These reactions produce N_2 gas and are the dominant mechanism for the loss of fixed N from the ocean (e.g., Hulth et al., 2005). Determining the magnitude of the marine fixed N sink is relevant to the global carbon cycle because the availability of fixed N limits primary production in most of the ocean (Smith, 1984; Tyrrell, 1999). Over the past decade, new measurements have fuelled debate over whether the fixed N budget is balanced in the modern ocean (Gruber, 2004; Codispoti, 2007). In particular, the rate of fixed N loss outside of the ocean's major oxygen minimum zones is crudely quantified, but globally significant (Codispoti, 2007). The coastal fixed N sink may be increasing as eutrophication expands the extent of intermittently and permanently anoxic waters and sediments (Larsson et al., 1985; Malakoff, 1998; Naqvi et al., 2000). The regular ventilation of Saanich Inlet makes it an ideal location to investigate the effects of deep-water renewal on fixed N loss as a model for other intermittently anoxic zones.

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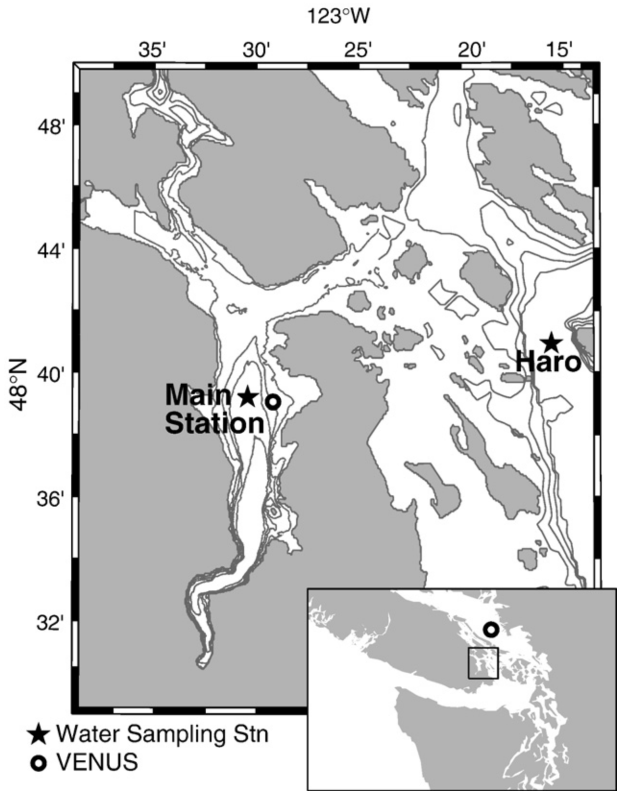

Fig. 1. Bathymetric map of Saanich Inlet and surrounding waters, showing the location of the VENUS CTD, the sampling station in Saanich Inlet, and the background station in Haro Strait. Contours represent 50 m depth intervals. Inset map shows the location of the VENUS CTD in the Strait of Georgia, along with the wider region of Vancouver Island, and coastal Washington state and British Columbia.

Until recently, the dominant process contributing to marine fixed N loss was thought to be denitrification, the sequential reduction of NO_3^- to N_2 and simultaneous oxidation of another compound such as organic matter (Devol, 2003). However, numerous studies have now confirmed the presence of anammox bacteria that use NO_2^- to anaerobically oxidize NH_4^+ to N_2 and have demonstrated that anammox dominates fixed N loss in some environments (Dalsgaard et al., 2003; Kuypers et al., 2003, 2005; Thamdrup et al., 2006). Quantifying fixed N loss from the N_2 excess is a relatively new method, reported for only two marine oxygen-deficient zones to date: the Arabian Sea (Devol et al., 2006) and the Black Sea (Fuchsman et al., 2008). This method requires no assumptions about the form of fixed N consumed, nor the process responsible. The N_2 excess we measure is derived from natural conditions in seawater and integrates over larger spatial and temporal scales than bottle incubations or benthic enclosures (Groffman et al., 2006), but cannot provide instantaneous rates. Our method estimates water-column N_2 production, along with any N_2 produced in the sediments that diffuses into the water column.

Mixing with adjacent oxygenated water impacts all anoxic zones, both by bringing new fixed N into the region and by redistributing chemicals within the basin. However, the timing, mechanisms, and ecological impacts of intrusion events are often poorly understood due to insufficient sampling (Berelson, 1991; Glazer et al., 2006; Pawlowicz et al., 2007a). Hannig et al. (2007) demonstrated that the dominant pathway to fixed N loss changed from denitrification to anammox over several years in response to an inflow event in the Gotland Deep, and Fuchsman et al. (2008) hypothesized that the extent of and pathways to fixed N loss may vary with time in the Black Sea. With a time series of measurements, we characterize the effects of multiple inflow events on fixed N loss rates at our location.

2. Methods

2.1. Study site and sampling apparatus

We collected ten CTD profiles at 48° 39′ N, 123° 30′ W (Fig. 1), close to the inlet mouth, between April 2008 and April 2009 using a SeaBird instrument with dissolved O_2 and photosynthetically active radiation (PAR) sensors. The station has a maximum depth of $\sim$190 m, while the sill is at 75 m. Discrete samples for measurements of N_2/Ar ratios, δ^{15}N–N_2, and dissolved O_2 concentration were collected in duplicate on nine of these cruises. In April 2009, we collected a profile of these measurements outside of Saanich Inlet in Haro Strait (347 m depth, 48° 41′ N, 123° 15′ W), where water-column fixed N loss does not occur. Gas samples were collected from 2-L Niskin bottles. A bucket with a spigot was used to collect surface samples starting in June 2008, in order to capture the extremely shallow mixed layer (often <1 m depth). Nutrient concentrations and the isotopic compositions of NO_3^- and NH_4^+ were measured by A. Bourbonnais for all dates where gas samples were collected and will be presented in a future publication.

2.2. Measurement of N_2/Ar ratios, δ^{15}N–N_2, and O_2 concentration

Dissolved O_2/N_2/Ar ratio and δ^{15}N–N_2 measurements were made following Emerson et al. (1999). Evacuated 185-mL glass flasks containing dried $HgCl_2$ were filled halfway with seawater, using tubing flushed with CO_2 to prevent air contamination. Flasks featured Louwers–Hapert valves with two sealing O-rings, and a vacuum was kept between the two O-rings before and after sampling (Hamme and Emerson, 2004b). After weighing, the water was equilibrated with the headspace and then removed.

The headspace gas was purified with a liquid N_2 trap, for complete removal of CO_2 and water vapor, and then analyzed on a stable isotope ratio mass spectrometer (IRMS). Isotope measurements are referenced to local air and corrected for isotopic fractionation between the water and headspace in the flasks (Knox et al., 1992). The precisions of N_2/Ar ratios and δ^{15}N–N_2 averaged $\pm 0.06\%$ and $\pm 0.01‰$ (per mil symbol needed), respectively, both based on duplicates.

Carbon monoxide in the IRMS ion source can positively bias δ^{15}N–N_2 measurements because CO has the same mass as N_2, but ^{13}C:^{12}C ratios are naturally higher than ^{15}N:^{14}N ratios. Removal of sample CO_2 by liquid N_2 eliminates this effect for most samples by preventing CO generation in the source (Bender et al., 1994), but does not remove CO naturally present in the sample. Carbon monoxide is photochemically produced in surface waters (Conrad and Seiler, 1980; Jones, 1991) and therefore may affect our δ^{15}N–N_2 measurements in the euphotic zone (upper 15 m on average, based on the depth of 1% surface incident irradiance from the PAR sensor). However, CO interference should not affect deeper samples, because CO is rapidly consumed at depth (Jones, 1991; Johnson and Bates, 1996). The presence of CO has a negligible effect on measured N_2/Ar ratios, since CO concentrations in natural waters are typically 4–6 orders of magnitude lower than N_2 concentrations (Conrad and Seiler, 1980; Jones, 1991).

Standards of known O_2/N_2/Ar ratios were used to determine chemical slope corrections caused by differences in ionization efficiencies when the sample and standard have different O_2 pressures (Emerson et al., 1999; Hamme and Emerson, 2004a). Samples from April through June 2008 were analyzed at the University of Washington on a Finnigan Delta-XL IRMS, and samples from July 2008 through April 2009 were analyzed at the University of Victoria on a Finnigan MAT 253 IRMS. Systematic offsets between the two labs of about 0.1% for N_2/Ar ratios and 0.05–0.10‰ for δ^{15}N–N_2 were observed between duplicate samples from another study site. These offsets may result from uncertainties in the ionization efficiency