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CARBON CYCLING AND REDOX CHEMISTRY IN AN ANOXIC MARINE BASIN, BRAS D'OR LAKE, NOVA SCOTIA

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ABSTRACT

Measurements of oxygen, methane, pCO_2, total dissolved inorganic carbon, total alkalinity, sulphide and nutrients were made in June, October and December 2017 in Whycocomagh Bay, a small marine basin at the western end of the Bras d'Or Lake estuarine system in Cape Breton, Nova Scotia. Dissolved oxygen was absent in the deep basin, similar to observations made in the years 1974, 1995-1997, and 2009-2021. Profiles of total dissolved inorganic carbon and total alkalinity were largely consistent with the sulphate reduction of particulate organic matter, having a Redfield stoichiometry of 106C:16N:1.6P. The concentration of dissolved methane ranged between 19-35 nmol L^{-1} (727-1147% saturation) above the thermocline, and reached 34.74 µmol L^{-1}, (931,900% saturation) in the deep anoxic zone. The potential rate of microbial methane oxidation at the base of the oxycline, determined from an incubation experiment, was 0.34 µmol L^{-1} d^{-1}, potentially acting to mitigate the flux of methane to the atmosphere. Deep water H_2S concentrations ranged from 747 to 1,074 µmol L^{-1}, more than a tenfold increase since the 1995-1997 study, with substantial increases also in ammonium and phosphate concentrations, likely as a result of eutrophication over the last two decades. Whycocomagh Bay presents an opportunity to study extreme marine redox chemistry at an easily accessible site.

Keywords: Anoxic, methane, carbon cycle, carbon dioxide

INTRODUCTION

Human-induced eutrophication of estuarine and shelf waters is causing an increasing frequency of hypoxia, defined as oxygen

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concentrations below 2 mg L^{-1} or 63 µmol L^{-1}, as a result of the bacterial respiration of organic matter (Rabalais *et al*. 2010). The progression of oxygen depletion to hypoxia causes detrimental effects to marine ecological systems, being fatal to most fin fish and epibenthic invertebrates (Diaz and Rosenberg 2008). Anoxic conditions lead to the formation of reduced chemical species such as ammonium and hydrogen sulphide, which can be toxic to fish and other forms of aquatic life depending on concentrations and pH (Randall and Tsui 2002, Podger 2013, Vaquer-Sunyer and Duarte 2010). Oxygen depletion due to respiration also results in the formation of high pCO_2 and low pH conditions that lead to increased dissolution of calcium carbonate skeletons (Nienhuis *et al*. 2010). In addition, hypoxic and anoxic regions are associated with enhanced emissions of methane and nitrous oxide, greenhouse gases that are much more potent than carbon dioxide (Naqvi *et al*. 2010, Etminan *et al*. 2016). A better understanding of the biogeochemical processes and biological implications of hypoxia and anoxia will contribute to more reliable environmental predictions of anthropogenic effects, including aquaculture and climate change.

Eutrophic coastal basins and inlets that are prone to seasonal or permanent oxygen depletion have provided conveniently accessible sites in which to study the effects of hypoxia and anoxia on ecology and biogeochemical element cycling e.g. Saanich Inlet, British Columbia: Matabos *et al*. 2012; Boknis Eck, SW Baltic Sea: Bange *et al*. 2009. Here we describe carbon cycling and related chemistry in an anoxic marine basin in the Bras d’Or Lake estuary, Nova Scotia. This site was previously sampled during oceanographic surveys in 1972-74 (Krauel 1975), 1995-97 (Strain *et al*. 2001), and 2009-2021 (DFO, 2021), providing a valuable baseline record of chemical conditions against which we can reference changes that have occurred over the last five decades.

STUDY SITE

Whycocomagh Bay is a semi-enclosed embayment that forms part of the inland estuarine system known as the Bras d’Or Lake (or “Lakes”). Geographically restricted water exchange between the Lakes and the NW Atlantic ocean, and the complexity of water circulation within the Lakes limits the tidal range in Whycocomagh Bay to <5 cm, (although winds and barometric set-up and runoff may add 15 cm to the amplitude), and the flushing time has been estimated at 2 years (Petrie and Bugden 2002). A 48 m deep basin at the western end of Whycocomagh Bay provides the focus of this study (Fig 1). It is connected to the rest of the Bay by a broad, 6.5 m deep sill to the east, and a narrow, 2.7 m deep channel between the shore and Indian Island to the north (Fig 1). The Skye River provides the major source of freshwater to this site, entering the basin through the northern channel. This geomorphology and circulation restrict vertical mixing in the basin, resulting in a pronounced pycnocline that separates a 10-12 m thick surface layer from a stagnant, oxygen-depleted bottom layer (Krauel 1975, Gurbutt and Petrie 1995, Petri & Bugden 2002). Anthropogenic sources of organic carbon to Whycocomagh Bay include a sewage treatment plant serving the community of Whycocomagh, discharging up to 750m^3 of effluent per day, and a Steelhead trout farm with 5 to 25 open mesh fish pens of 20 m diameter deployed within the basin since 2011 (Fig 1).

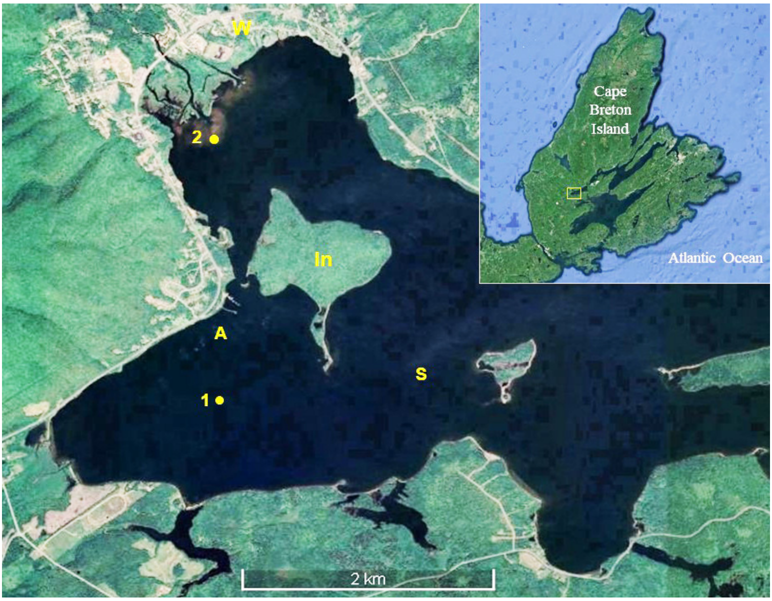

Fig 1 **The Whycocomagh Basin study area and location on Cape Breton Island, Nova Scotia (inset). Sample Site 1 (45.9460 °N, 61.1250 °W) lies above the centre of the deep basin while Site 2 (45.9648 °N, 61.1261 °W) is at the mouth of the Skye River. The community of Whycocomagh (W), Indian Island (In) and the approximate location of the aquaculture pens (A) and sill (S) are also indicated.**

METHODS

Water sampling was done in the centre of the basin (47.5 m depth, Fig 1) from a small vessel equipped with a winch on June 27, October 3, and December 4 and 5, 2017. Samples were collected at 8 depths in June and 9 depths for dissolved methane/pCO_2, oxygen, pH, total dissolved inorganic carbon (TIC)/total alkalinity (TA), hydrogen sulphide (H2S), and nutrients determinations in that order using 5 L Niskin bottles in conjunction with a SeaBird CTD (SBE-25 with oxygen). Water samples were also collected for a microbial methane oxidation (MOx) experiment. Additional samples were obtained from a site at the mouth of the Skye River on the 5th December 2017.

Dissolved oxygen, methane, carbon dioxide and ammonium

Samples for dissolved oxygen were drawn into gravimetrically calibrated 125 mL iodine flasks and immediately fixed by the addition of Winkler reagents, then stored in the dark until analysis within 24 hours. Dissolved oxygen concentrations were determined using a computer controlled Winkler titration with colorimetric endpoint detection after Jones *et al.* (1992). Oxygen saturation was calculated using the Bunsen solubility coefficients of Weiss (1970).

Dissolved methane and pCO_2 samples were collected in 125 mL serum bottles, preserved by the addition of mercuric chloride, and immediately crimp sealed with butyl rubber septa. CH_4/pCO_2 were later measured with a static headspace equilibrium method modified from Neill *et al.* (1997) where equilibrated headspace samples were injected into a gas chromatograph equipped with a catalytic methanizer and a flame ionization detector. Methane saturation was calculated using the Bunsen solubility coefficients of Weisenburg and Guinasso (1979). Total sulphide ($H_2S + HS^- + S^{2-}$) was determined within 24 hours of sample collection using the spectrophotometric methylene blue method of Cline (1969). H_2S, HS^- and S^{2-} are indistinguishable with this method and henceforth will be collectively referred to as H_2S.

CO_2 parameters

Total dissolved inorganic carbon (TIC) was measured according to Dickson *et al.* (2007) by purging acidified water samples with a stream of high purity nitrogen in an automated gas extraction system, the dried gas stream being analysed for carbon dioxide by coulometry. Total alkalinity (TA) was analysed by an automated open cell potentiometric titration with 0.1 N hydrochloric acid after Dickson *et al*. (2007). Seawater pH on the total hydrogen ion scale was determined at 25 ± 0.05 °C by a spectrophotometric method with purified m-cresol purple (Clayton and Byrne, 1993). Results for TIC, TA and pH were calibrated with measurements of a certified seawater reference material supplied by Andrew Dickson (Scripps Oceanographic Institution, San Diego, USA). pH and pCO_2 values were corrected to in-situ conditions of temperature and pressure using the CO2.SYS macro for Microsoft Excel (Lewis and Wallace 1998) with TIC as a second carbonate parameter and correcting for the effects of sulphide and ammonium.

Nutrients

Nutrient samples were measured with a segmented flow auto analyser following the methods described in Strickland and Parsons (1972) for nitrate, phosphate and silicate, and the fluorometric method of Kerouel and Aminot (1997) for ammonium. Reliable nitrate measurements are not available for the anoxic water owing to high levels of sulphide that interfere with the cadmium reduction method.

RESULTS AND DISCUSSION

Temperature and salinity

The upper 15 m of the water column displayed a wide seasonal variation in temperature, the surface water (1 m depth) ranging from 18.6 °C in June to 4.8 °C in December (Fig 2a-2c). Surface warming during summer and associated deepening of thermocline were followed by autumn cooling and wind mixing events, which seemed to cause the temperature inversion at 5-8 m in October. Continued cooling and more gradual mixing seemed to cause the inversion at 7-19 m in December. Below 23 m, the temperature remained constant at 3.16 °C during the three visits (Fig 2a). Surface and deep water conditions were similar to those recorded during 1996 and 1997 (Strain *et al*. 2001). In the latter case, bottom water temperature was in the range 2.94-3.23 °C, so it appears that warming of the deep basin has not occurred since then. However, slightly lower deep water temperatures (1.80-3.00 °C)

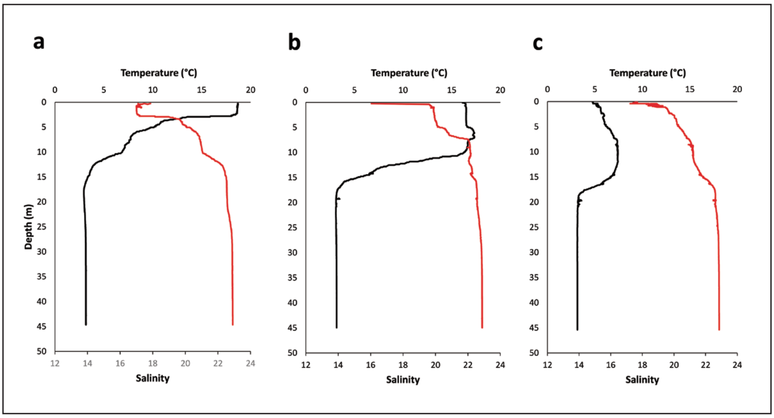

Fig 2 **CTD profiles of temperature (black line) and salinity (red line) in the Whycocomagh Basin measured in a) June, b) October, and c) December 2017.**

were reported in 1970's (Krauel 1975), so there may have been a small increase in the past.

In the case of salinity, freshening of the deep water mass is apparent, with 2017 values of 22.85 compared to 23.05-23.07 in 1996-97 (Strain *et al.* 2001), and 22.70-24.9 in 1972-74 (Krauel 1975). No sampling was undertaken in any study during January to April when ice typically forms over the northern Bras d'Or lakes, with the greatest extent of ice cover typically occurring in early March (Petrie and Bugden 2002).

Dissolved oxygen

The extent of molecular oxygen penetration into Whycocomagh Basin was at its greatest in June when the base of oxycline reached a depth of about 23 m (Fig 3a). A broad subsurface maximum of 352 µmol L^{-1} (106% saturation) at 10 m depth suggested a zone of maximal photosynthetic activity. A very similar profile was seen on June 2nd, 1997, where oxygen concentrations reached a maximum of 370 µmol L^{-1} at 10 m (Strain *et al.* 2001). A curious feature of the June profile was a small secondary peak at 19.5 m, potentially a result of low light photosynthesis. In October, the oxycline had retreated upwards to 14 m but with a sub-oxic zone extending down to about 19 m, and there was a near-surface maximum of 245 µmol L^{-1} (Fig 3b). This pattern continued in December but with increased concentrations throughout the upper 19 m, to a near-surface

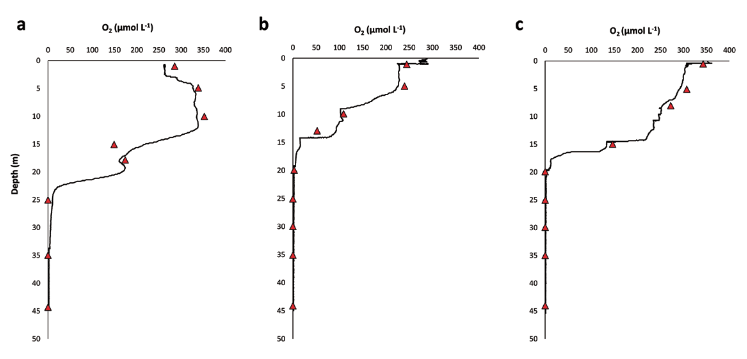

Fig 3 **The distribution of dissolved oxygen in the Whycocomagh Basin on 27th June (a), 3rd October (b) and 4th December (c), 2017. The solid black lines show CTD oxygen sensor profiles while red triangles represent Winkler measurements.**

maximum of 343 µmol L^{-1} (Fig 3c). At no time during the 2017 surveys could molecular oxygen be detected at 25 m or deeper. This finding is in agreement with the 1972-74 (Krauel 1975) and 1996-1997 (Strain *et al.* 2001) oxygen data, as well as with data from more than 80 profiles collected since 2009 (Hatcher, unpublished data). This deep basin has been continuously anoxic for half a century at least.

Carbonate system

The distribution of the carbonate parameters, TIC and TA, in gravimetric units of µmol kg^{-1}, plus pCO_2 and pH values corrected to in situ temperature and pressure, are shown in Fig 4. The concentrations of TIC and TA in the deep water were about two-fold higher than in the upper 20 m, while pCO_2 reached 6,665 µatm, or around 1,626% saturation based on an atmospheric mole fraction of 400 ppm. In the surface oxygenated water, TIC is controlled by the removal or addition of carbon dioxide resulting from the opposing effects of photosynthesis and respiration. About 1% of dissolved carbon dioxide reacts with water to form carbonic acid, H_2CO_3 which dissociates to form HCO_3^- that is in turn in equilibrium with CO_3^{2-} at a given pH. In either case, carbonate alkalinity (CA) is unaffected as the charge balance between protons and anions is maintained. The question therefore arises as to why TIC, and indeed pCO_2, is so high in the deep water in the absence of aerobic respiration. The underlying geology of the region may play a role in influencing TA as, prior to inundation through sea level rise, the Bras d'Or Lakes was a series of lakes and river channels carved through the Carboniferous Windsor Group, soft sedimentary rocks comprised of limestones and evaporates (Shaw *et al.* 2002). However, the distribution of carbonate species and H_2S can be satisfactorily explained by the anaerobic process of dissimilatory sulphate reduction.

In the absence of oxygen, microbial respiration of particulate organic matter proceeds with a stepwise utilisation of alternative electron acceptors according to their energy yield *i.e.* NO_3^-, iron and manganese oxides, SO_4^{2-} and finally, carbon. Although there were no reliable nitrate measurements from the deep basin owing to the high levels of sulphide, the concentration is presumably very low owing to removal by the denitrification pathway which proceeds via nitrite, nitric oxide and nitrous oxide to nitrogen gas:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

The reduction of particulate organic matter generally proceeds mainly through sulphate reduction owing to the relatively high abundance of SO_4^{2-} compared to other electron acceptors. The sulphate reduction of organic matter having a Redfield Ratio of 106C: 16N: 1P can be represented by the following general equation from Richards (1965):

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53SO_4^{2-} \rightarrow$$

$$106HCO_3^- + 53H_2S + 16NH_3 + H_3PO_4$$

Hence, according to Hiscock and Millero (2006), the stoichiometric relationships between TA, TIC and H_2S can represented by the equations:

$$\frac{\Delta TA}{\Delta H_2S} \approx \left(\frac{106+16-2}{53}\right) = 2.3$$

$$\frac{\Delta TIC}{\Delta H_2S} \approx \left(\frac{106}{53}\right) = 2.0$$

$$\frac{\Delta TA}{\Delta TIC} \approx \left(\frac{106 + 16 - 2}{106}\right) = 1.13$$

For the Whycocomagh Bay anoxic zone, linear least square correlations for the measured parameters, with H_2S concentration corrected to gravimetric units of µmol kg^{-1} to match TIC and TA, shown above return slopes of 2.36 ($R^2 = 0.85$) for TA:H_2S, 2.05 ($R^2 = 0.88$) for TIC:H_2S and 1.15 ($R^2 = 0.97$) for TA:TIC, in excellent agreement with the theoretical relationships. Sulphate reduction can therefore largely explain the observed distribution of TIC and TA below the oxycline.

An interesting feature of the pCO_2 and pH time series is the increasing trend in pCO_2 at 20 m, from around 2,000 µatm in June to 5,491 µatm in December, with the development of a pronounced shoulder in the pCO_2 profile in October (Fig 4). The increase in pCO_2 was accompanied by a fall in pH to a minimum value for the year of 6.958 at 20 m depth in December (Fig 4). This is also the depth at which molecular oxygen first appears in the anaerobic/aerobic transition zone and the potential cause for this increase in pCO_2 is discussed later.

Dissolved methane, sulphide and ammonium

In the event that SO_4^- and the more energetically favourable electron acceptors become depleted, the reduction of organic carbon can only proceed by methanogenesis. The two perhaps most common pathways in the natural environment involve the reduction of carbon dioxide and acetate by methanogens, a group of obligate anaerobes belonging to the *Archaea* (Fenchel *et al.* 2012):

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

$$CH_3COOH \rightarrow CH_4 + CO_2$$

Methane is of particular interest as it is a potent greenhouse gas with a global warming potential of about 80 times that of CO_2 over a 20 year time frame (Myhre *et al.* 2013). Shelf seas and estuaries hold a disproportionate importance in the global sea/air flux and it has been estimated that these regions, accounting for only about 16% of the global ocean area, may contribute 75% of total marine CH_4 emissions (Weber *et al.* 2019, Rosentreter *et al.* 2021).

Surface CH_4 concentrations were in the range 19-35 nmol L^{-1} (727-1,147% saturation) and a curious sub-surface maximum was observed in the October and December profiles (Fig 5b). The source

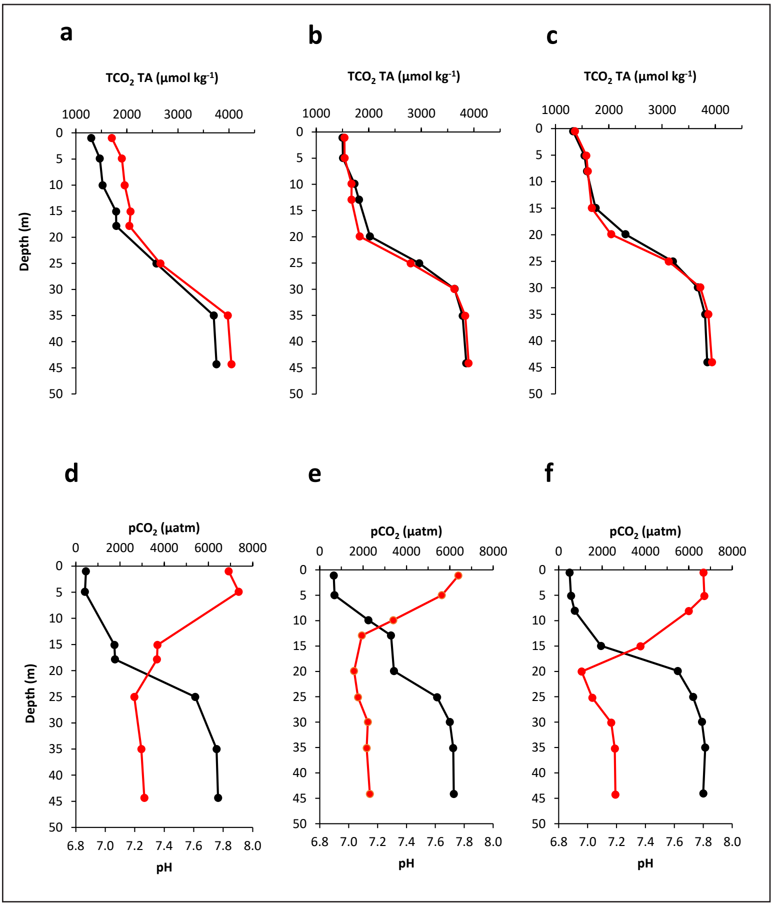

Fig 4 **The top row shows profiles of total dissolved inorganic carbon (black) and total alkalinity (red) in the Whycocomagh Basin on June (a), October (b) and December (c), 2017. The bottom row shows profiles of pCO_2 (black) and pH (red) on June (d), October (e) and December (f).**

of this maximum is not clear, and they coincide approximately with the sub-surface temperature inversions (Fig 2b & 2c). In order to assess the fresh water source of methane, the mouth of the Skye River was sampled and had a concentration of 57.4 nmol L^{-1} (1,658% saturation), hence riverine CH_4 input contributes to CH_4 supersaturation in the surface water of Whycocomagh Bay.

Dissolved methane concentrations in the deep anoxic water were astonishingly high, approaching one million percent saturation (range: 31.40-34.74 μmol L^{-1}, 844,896-931,909% saturation).

These concentrations are a factor of 10 higher than those seen in the permanently anoxic marine waters of the Black Sea and Cariaco Basin (Kessler and Rheeburg 2006), although still below the highest levels measured in deep freshwater lakes (e.g. Blees *et al*. 2014). Above 30 m, the concentration declined steeply by a factor of 1,000 (Fig 5). Processes responsible for this pattern may include diapycnal transport driven by the CH_4 concentration gradient with subsequent advection and release to the atmosphere, and microbial oxidation (MOx) by methanotrophic bacteria.

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

In this study, the CH_4 concentration gradients lie rather lower than the pycnocline and seem to be more associated with the depth where molecular oxygen first makes an appearance. This is consistent with removal by methanotrophy, as the study of Steinle *et al*. (2017) showed that MOx rates in the western Baltic Sea were optimal at sub micro-molar O_2 concentrations.

Potential rate of methane oxidation

On the final visit to Whycocomagh Bay in December, water was sampled for an incubation experiment to investigate the rate of microbial methane oxidation at the base of the oxycline.

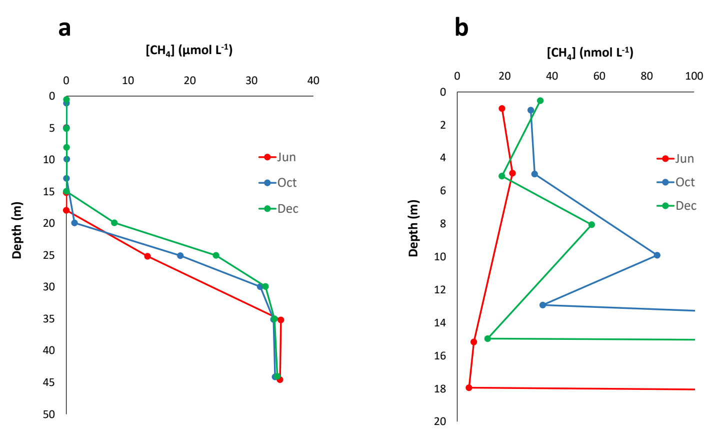

Fig 5 **(a) Dissolved methane concentrations (µmol L^{-1}) in the Whycocomagh Basin in June, October and December 2017. (b) Surface concentrations of methane (note the unit: nmol L^{-1}).**

Repeated casts to the 16-18m depth range were made with a 5 L Niskin bottle and the water transferred to an acid rinsed 20 L glass carboy. Some degree of gas exchange between the water and atmosphere was inevitable during the transfer process, hence the oxygen concentration *in vitro*, later determined to be 109 µmol L^{-1}, was almost certainly higher that the *in situ* concentration, and so the measured rate should be regarded as a potential one (i.e. not limited by oxygen availability). The carboy was transported to the laboratory and the water subdivided by siphoning into sixteen, 125 mL serum bottles, half of which were poisoned by the addition of mercuric chloride. The bottles were incubated in the dark at *in situ* temperature, and a pair of poisoned and non-poisoned samples were analysed for dissolved methane at intervals. The non-poisoned time series showed a linear decline in methane concentration of around 50% over the initial 24 hours, a loss rate of 0.34 µmol L^{-1} d^{-1} (Fig 6). This value is much higher than that measured in a coastal inlet in the south-western Baltic Sea using the similar method, ranged from 1.0-11.6 nmol L^{-1} d^{-1} (Steinle *et al.* 2017). However, multiple environmental factors can affect the methane oxidation rate,

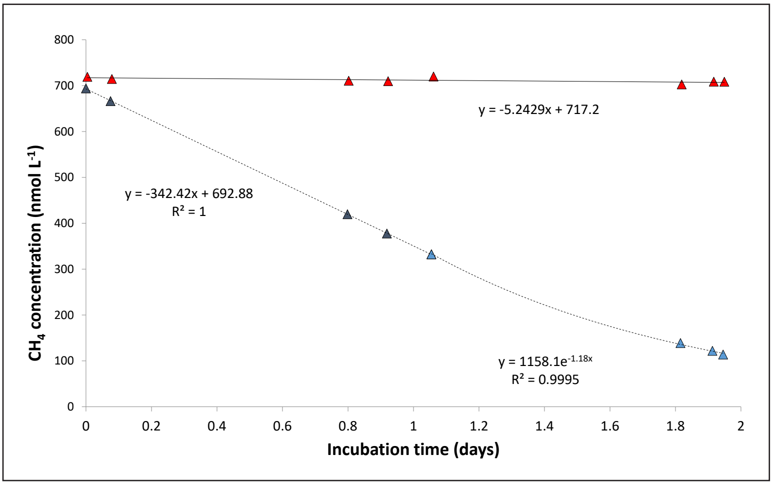

Fig 6 **A two day series of incubation measurements of methane subsamples drawn from a bulk water sample collected from the base of the oxycline at Site 1 in the Whycocomagh Basin on the 5th of December, 2017. Red triangles represent poisoned subsamples, blue triangles show non-poisoned samples. A linear regression was fitted to the entire poisoned data set, and to the initial 24 hours of non-poisoned data, whereas the subsequent measurements were best represented by an exponential fit.**

including oxygen concentrations and water temperature, therefore the direct comparison requires caution. Measurements in the second day of incubation indicate that methane removal had entered a non-linear phase, with an exponential regression offering the best fit. This transition from zero order (independent of substrate concentration) to first order (concentration-dependent) kinetics may reflect the substrate handling capacity of the bacterial population.

The emerging picture of methane dynamics in Whycocomagh Bay is one of intense microbial oxidation activity in the hypoxic zone that potentially acts as a filter to limit the transfer of methane into the surface mixed layer and thus mitigate atmospheric release (Steinle *et al.* 2017). This process may explain the persistent pCO_2 sub-surface maximum at around 20 m depth observed through the year, a result of the conversion of dissolved methane to carbon dioxide. This model also raises the question of the degree to which this form of chemolithotrophic primary production in the water column, independent of light availability, can support higher trophic levels, analogous to cold seep biomes.

Sulphide and ammonium are the terminal products of sulphate and nitrate reduction. In the absence of a suitable electron acceptor, H_2S and NH_4^+ will accumulate in stagnant anoxic environments, but unlike methane, they are toxic in high concentrations to vertebrates and invertebrates, and may have a detrimental effect on aquaculture operations and fisheries. The seasonal distributions of sulphide and ammonium are shown in Fig 7.

H_2S was always undetectable in the well oxygenated surface water, yet abundant in the hypoxic or anoxic water present below around 20 m depth in the central basin. In the bottom water (44 m), sulphide concentration increased during the course of the year from 734 $\mu mol\ L^{-1}$ in June to 841 $\mu mol\ L^{-1}$ in October and on to 1,047 $\mu mol\ L^{-1}$ in December. This increase is likely related to an annual cycle in organic matter input in which case, in order to maintain a quasi-steady state from year to year, the 70% increase in sulphide from June to December would have to be balanced by a net loss during the winter months. Physical loss processes include diffusion across the oxycline where H_2S undergoes spontaneous chemical oxidation in oxygenated seawater, a first order reaction with a H_2S half-life of around one day (Zhang and Millero 1993). H_2S may also be consumed in the absence of oxygen by photosynthetic purple

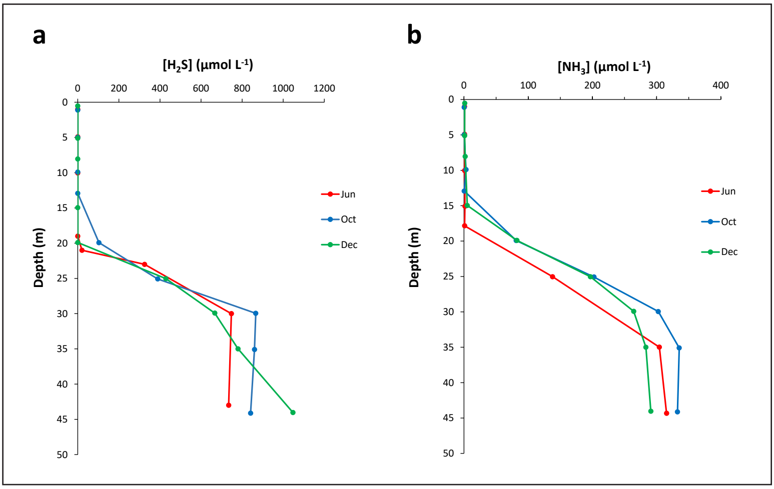

Fig 7 Profiles of (a) total sulphide (H_2S), and (b) ammonia concentrations in the Whycocomagh Basin in June, October and December 2017 (Dates as in Fig 3).

sulphur bacteria, and in the presence of oxygen by sulphur oxidising bacteria such as *Beggiatoa* (Jørgensen *et al.* 2010). The significance of these microbial pathways at this site is not yet known, but imaging with a drop camera and ROV shows a distinct pseudo benthos (Siebrth 1987, Ott and Herndl, 1992) at 16.5 m depth in the water column, and a dense band of *Beggiatoa* on the seabed perimeter of the Whycocomagh basin between 15 and 19m depth. (Hatcher, unpublished data).

The distribution of ammonium (NH_4^+) was similar to that of dissolved methane, with high concentrations below 30 m and low concentrations in the upper 15 m of the water column (Fig 7). Bottom water values remained fairly stable, fluctuating between 315.5 µmol L^{-1} in June, 332.5 µmol L^{-1} in October and 291.0 µmol L^{-1} in December. Unsurprisingly, surface water values were much lower given that ammonium is a preferred source of nitrogen for phytoplankton, ranging from 0.4 to 1.1 µmol L^{-1}. In anoxic marine environments, ammonium is produced by the bacterial process of ammonification, i.e. the microbial deamination of organic matter where ammonium is a metabolic product. A further source of ammonium is dissimilatory nitrate reduction to ammonium, with nitrate as an electron acceptor. The latter pathway is often coupled across the anaerobic/aerobic interface with the oxidation of ammonium to nitrite, i.e. the first stage of nitrification where nitrous oxide is released as a by-product (Pajares and Ramos 2019). Although nitrous oxide concentrations were not measured in the study, it is highly likely that Whycocomagh Bay is a strong source of this powerful greenhouse gas.

A comparison of these data with 1996-1997 measurements of sulphide and ammonium reveals a striking contrast. Strain *et al.* (2001) reported deep water values in Whycocomagh Bay of 30-62 µmol L^{-1} H_2S and 66-136 µmol L^{-1} NH_4^+. The subsequent, twenty year interval has therefore seen more than a tenfold increase in sulphide and around a threefold increase in ammonium, suggesting a trend of increasing eutrophication.

Phosphate and silicate

Distributions of phosphate and silicate for 2017 are shown in Fig 8. In both cases there was a shoaling of the nutricline as the year progressed. The bottom water phosphate concentration was relatively stable throughout 2017, remaining between 36.1-37.6 µmol L^{-1}. Organic phosphate contained in particulate organic matter will be regenerated during dissimilatory sulphate reduction. A plot of H_3PO_4 vs TIC in anoxic water had a slope of 0.015, i.e. a C:P ratio of 106:1.6, which is rather higher than the standard Redfield Ratio given in Eqn. 2. This may reflect the influence of terrestrial runoff or a higher C:P ratio in anthropogenic discharges compared to particulate organic matter resulting from *in situ* photosynthesis.

Bottom water silicate concentration also varied slightly, ranging from 154.9 to 162.3 µmol L^{-1} (Fig 8) and the profile also showed a classic pattern of surface uptake and deep water regeneration. The source of silicate to the Bras d'Or Lakes is likely to be primarily through rock weathering and freshwater runoff, while deep water enrichment can be caused by the transfer of silica in sinking diatoms, although one cannot rule out accelerated dissolution of silicic sediments in the low pH anoxic zone. Redfield stoichiometry for diatoms has been expanded to include silica with a mean Si:C ratio of 0.13 being reported for a range of cultures (Brzezinski 1985). These results yield a Si:C ratio of 0.062 in anoxic water, which is consistent with some fraction of the total organic matter supplied to the deep basin being comprised of diatoms.

In the 1995-1997 study of Whycocomagh Bay, the deep water concentrations were 9.2-14.0 µmol L^{-1} for H_3PO_4 and 37-85 µmol L^{-1}

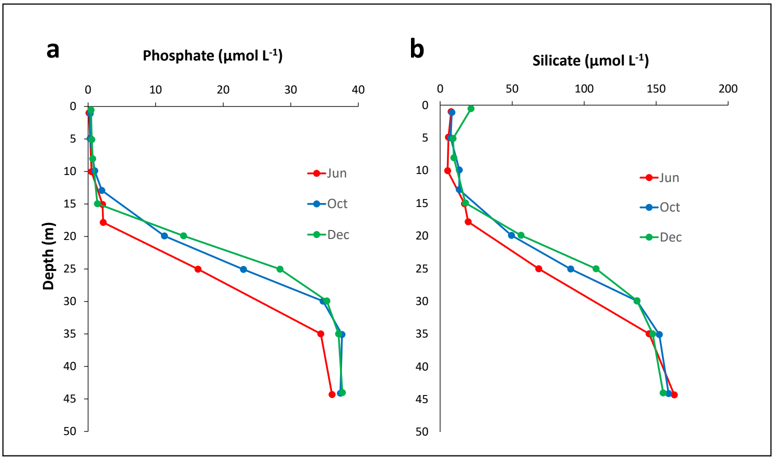

Fig 8 **Profiles of a) phosphate and b) silicate concentration through the water column measured at Site 1 in the Whycocomagh Basin in June (red), October (blue) and December (green). (dates as in Fig 3).**

for $Si(OH)_4$ (Strain *et al.* 2001). These more recent measurements show at least a two fold increase for these nutrients, again suggesting ongoing eutrophication.

Summary of biogeochemical processes

Fig 9 illustrates a simple model of the major biogeochemical pathways relevant to the compounds measured in this study. Particulate organic carbon comprised of marine and terrestrial organic matter sinks down to the water/sediment interface. Anaerobic decomposition and remineralisation proceeds largely by sulphate reduction, with the release of bicarbonate, hydrogen sulphide, ammonium, phosphate and silicate, while methanogenesis releases both methane and carbon dioxide to the water column. These products diffuse into the hypoxic layer between around 15 to 20 m depth where ammonium, hydrogen sulphide and methane are vigorously oxidised, the upward flux of these compound being balanced by a downward flux of molecular oxygen. Hydrogen sulphide is completely removed in this layer, being absent in the oxygenated surface water. The remaining gases and nutrients escape to a greater or lesser degree into the surface layer and provide the requirements for photosynthesis while supersaturated levels of methane and carbon dioxide drive a sea to air flux of these gases.

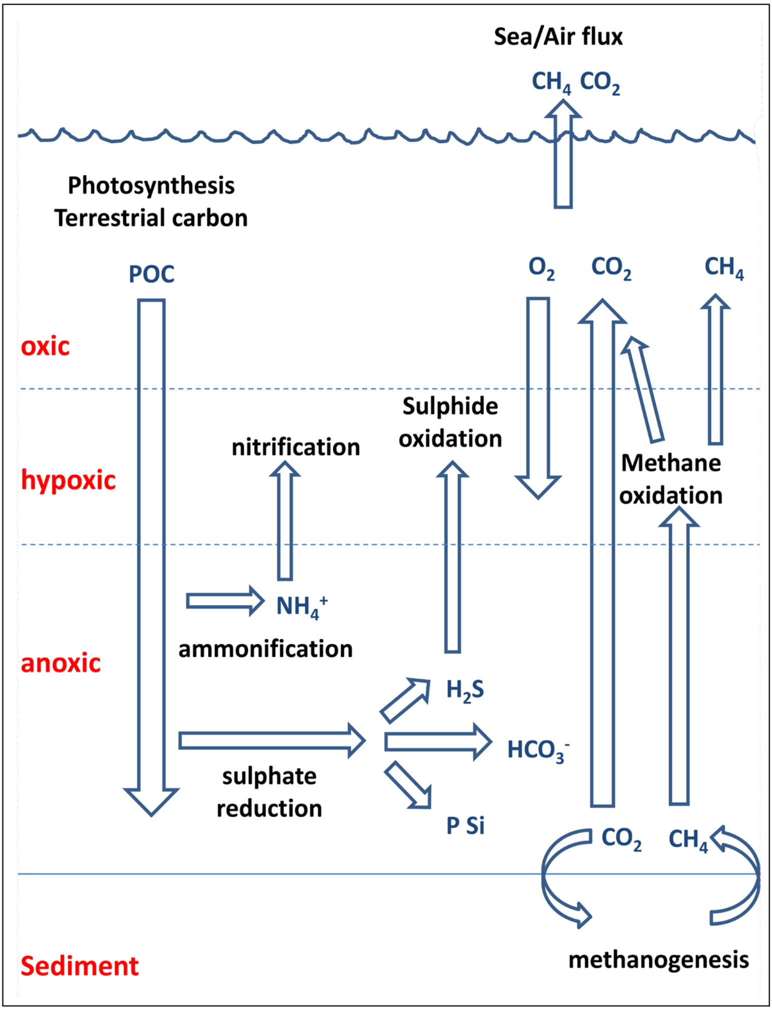

Fig 9 **A simplified diagram of the major relevant biogeochemical pathways in the Whycocomagh Basin, Bras d'Or Lake, Nova Scotia.**

CONCLUSIONS

The basin in Whycocomagh Bay, Bras d'Or Lakes, with a likely state of permanent anoxia in the deep water, provides a unique and easily accessible site where elemental redox processes can be conveniently studied. The hypoxic/anoxic cycling of organic carbon is of particular interest. Distributions of the dissolved carbon dioxide parameters TIC and TA in the anoxic zone can be explained by sulphate reduction of particulate organic matter with a Redfield C:N:P ratio of 106:16:1.6. Although the concentration of dissolved methane accumulating as a result of contemporary methanogenesis is among the highest recorded in a marine basin, the very high potential rate of microbial methane oxidation at the base of the oxycline suggests that this is substantially mitigating the atmospheric release of CH_4. This hypothesis is supported by a co-occurring pCO_2 maximum in the hypoxic zone. It would be worth making further, fine scale measurements of MOx rate through the well-defined oxycline to investigate its dependence on substrate concentrations. Also, it would be of interest to find out if this chemolithotrophic activity is supporting higher trophic levels through the grazing of methanotrophic bacteria by microzooplankton.

A comparison with sulphide and nutrient data obtained here two decades ago show a tenfold increase in H_2S, a threefold increase in ammonium and a doubling in phosphate concentration in the stagnant deep water. This is strong evidence of eutrophication, presumably resulting from, or enhanced by, anthropogenic sources of particulate organic matter from nearby sewage discharges and from aquaculture operations in the bay. In this regard, the chemical conditions pertaining to Whycocomagh Bay may be an analogue for larger perturbed estuaries.

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