

Hidden biogeochemical anonymities under Antarctic Fast Ice

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Abstract:

Climate change is negatively affecting the extent of summer sea ice and the global oceanic oxygen concentrations, it is therefore imperative to decipher the life processes under the Antarctic fast ice. The biogeochemical parameters like dissolved oxygen, inorganic carbon, macronutrients, phytoplankton, and chlorophyll *a* (Chl *a*) were studied under the fast ice (by drilling ~1.8 m thick ice) around Larsemann Hills, East Antarctica during India's Scientific Expedition to Antarctica (31st ISEA-2011/12 and 33rd ISEA-2013/14). The waters under ice cover were characterized by hyperoxia (up to 10.6 ml/L). Macronutrient concentrations under sea ice were depleted (<0.1 μM NO_3 , PO_4 and <2 μM SiO_4); this could be ascribed to the nutrient demand from under ice algae. The water under the ice cover exhibited higher algal biomass (Chl *a* up to 6.1 mg/m^3) and CO_2 under saturation (pCO_2 <10 μatm). This is reflected through the Spearman rank correlation indicating a negative correlation between Chl *a* and pCO_2 ($r = -0.41$). The strong negative correlation between dissolved oxygen and pCO_2 ($r = -0.67$) suggests that photosynthesis regulates the concentrations of both these climatically important gases. The waters under the sea ice cover had brownish mucilaginous aggregates comprised of tube-forming diatoms *Berkeleya adelienses* and *Nitzschia lecointei*. These unusual biogeochemical changes were seen only at the ice water interface, and not at deeper depths. This study suggests that with global warming and sea ice melting, Antarctica might witness phytoplankton community shifts.

Keywords: Sea ice, pCO_2 , chlorophyll, biogeochemistry, Antarctica

1. Introduction

Climate change has shown effects like the decline in global oceanic oxygen concentrations in the past few decades (Schmidtko et al., 2017) concomitant with a decreasing summer sea ice extent in the Arctic and some areas of Antarctic in the recent decades. Antarctic sea ice represents one of the largest and most dynamic ecosystems of the world ocean. The seasonal sea ice advance and retreat is an important factor for an effective functioning of the Antarctic marine food web (Murphy et al., 2016). Annually the sea ice expands and extends to cover over 20 million km² of the Southern Ocean (Legendre et al., 1992). Under the snow and sea ice cover lies a unique habitat for bacteria, diatoms, autotrophic flagellates, heterotrophic flagellates, ciliates and metazoans that are enclosed in an ice matrix (Garrison and Buck 1989; Thomas and Dieckmann 1992).

The snow and ice cover reduces most of the light available for phytoplankton production, however this unique ecosystem provides a stable habitat for algal blooms. The sea ice algae contribute ~20% of the primary productivity beneath the ice cover (Legendre et al., 1992) and could significantly affect the biogeochemical cycles of the entire Southern Ocean (Smith and Nelson 1986). The coastal and shelf waters around Antarctica exhibit high rates of primary productivity (Smith and Nelson 1986) and possibly constitute an important sink for atmospheric CO₂ (Smith et al., 2000; Arrigo et al., 2008). The sea-ice habitat is also a major contributor to global sulphur and carbon cycles (Trevena et al., 2003; Semiletov et al., 2004; Zemmelen et al., 2005, 2006)

Light is considered as a limiting factor for productivity beneath the ice cover (Palmisano et al., 1985; Cota and Smith 1991), however, there is a considerable evidence for shade adaptation (Palmisano et al., 1985; Lizotte and Sullivan 1991). A recent study by Assmy et al. (2017) reported that leads in the ice cover can provide additional sunlight necessary to initiate and sustain the phytoplankton bloom. Moreover, sea ice diatoms like *Fragilariopsis cylindrus* tend to have allelic divergence for adaptation in fluctuating environments (Mock et al., 2017). While much of the emphasis is given to the sea ice biogeochemistry, the studies highlighting biogeochemical processes and colonisation by micro biota beneath the land fast sea ice needs documentation. The aim of this study is to explore and record the pristine environment propagating beneath the land fast sea ice and to understand the phytoplankton community adaptable beneath the sea ice cover.

2. Material and Methods

2.1 Sampling

The present study was carried out in the Larsemann Hills region of East Antarctica, near the Indian Antarctic Research base 'Bharati' (Fig.1). The fast ice was drilled up to -1.8 m depth (~30 cm

diameter hole) using a Jiffy auger drill in the Quilty Bay region, Larsemann Hills, East Antarctica during the 31st and 33rd Indian Scientific Expedition to Antarctica (ISEA-January 2012 and 2014). During the 31-ISEA, surficial water at the ice water interface was collected, whereas during the 33-ISEA, vertical profiles were collected till the bottom (~160 m). The vertical distribution of biogeochemical parameters was carried out at nine stations near the Quilty Bay. Sampling at each station was at the surface, 35m, 65m, 115m, and 160m. The water-depth in the Quilty Bay was measured manually using a marked rope and it varied from 38 m to 160 m. Niskin samplers were used for sampling water, by passing it through the drilled hole in sea ice.

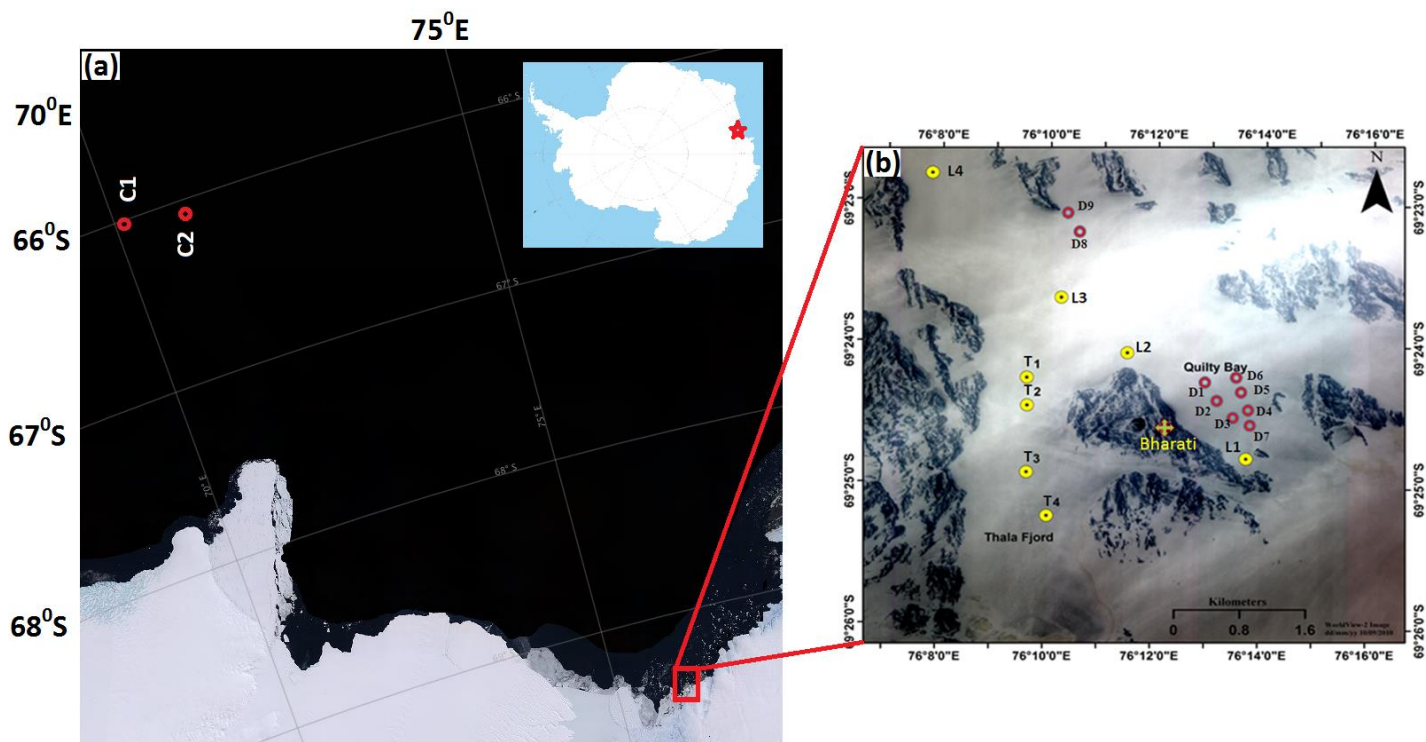


Figure 1: (a) Location of the study area in East Antarctica. C1 and C2 stations which represent non ice covered waters. The red box shows the location of sampling points. This map is generated using Landsat Image Mosaic of Antarctica (LIMA) (b)The set of sampling locations marked by the red box is plotted on very high-resolution World View-2 satellite imagery of Quilty Bay, East Antarctica. Yellow and red dots symbolize stations covered during 2012 and 2014, respectively.

2.2 Physicochemical parameters

Salinity was measured using an Autosol during 31-ISEA and using EUTECH PC 700 during 33-ISEA. Dissolved Oxygen was estimated following the Winkler titrimetric method (Grasshoff et al., 1983). Nutrients (silicate, phosphate, nitrate and nitrite) were measured using a Skalar Autoanalyzer by standard colorimetric method (Grasshoff et al., 1983). The standard deviation for duplicates was 0.06 μM for silicate, 0.05 μM for nitrate, 0.01 μM for nitrite and phosphate. Total carbon dioxide

(tCO₂) content of seawater samples was determined using a coulometer (model 5014 of U.I.C. Inc., USA). The reliability of the coulometric titration was regularly checked with certified referenced materials (CRMs, Batch # 92) provided by Prof. A. Dickson (SIO, University of California). The pH_T was measured at 25°C by cresol red spectrophotometry (Byrne and Breland 1989). The pH_T was then corrected to the in-situ temperature following the equation of Gieskes (1969). The analytical precision was about ±2 μM for tCO₂ and ~0.003 for pH. In situ pCO₂ was calculated using the dissociation constants of Dickson and Millero (1987).

2.3 Biological parameters

For Chl *a* measurement, 5 litre seawater was filtered on 0.7 μm pore size 47mm polycarbonate filters at low vacuum. The pigments were extracted from the phytoplankton in 90% acetone with the aid of a mechanical tissue grinder and allowed to settle for a minimum of 2 h, but not to exceed 24 h, to ensure thorough extraction of the chlorophyll *a*. The filter slurry was centrifuged for 15 min to clarify the solution. An aliquot of the supernatant was transferred to a glass cuvette and fluorescence was measured on fluorometer (Model 10-AU, Turner Designs) before and after acidification to 0.003 N HCl with 0.1 N HCl. Sensitivity calibration factors, which have been previously determined on solutions of pure Chl *a* of known concentration, are used to calculate the concentration of Chl *a*.

For phytoplankton analysis, surface water (minimum 8L) was filtered through 10 μm mesh (Hydrobios, Kiel, Germany) and preserved in 10% buffered formaldehyde solution until analysis. Phytoplankton (>10μm) abundance was determined using a Nikon Eclipse Inverted Microscope at 20x magnification, following the techniques of Uthermöhl (1958).

2.4 Sea Ice Thickness (SIT)

SIT was measured manually using a steel scale that was dipped into the drilled hole till the edge of the sea ice.

2.5 Statistics

Spearman rank correlation was run between various biogeochemical parameters, in order to understand the correlation between various parameters.

3. Results

3.1 Variability in Sea Ice Thickness (SIT)

The SIT was greater than 1 m during both the sampling years. SIT was more towards the continent as compared to the marine waters. The SIT during 2012 ranged from 1.29 to 1.62m, while it ranged

from 1.16 to 1.76 m during 2014 (Table 1). The average SIT during 2012 was 1.52 m while during 2014 was 1.39 m.

Table 1: Variations in Sea Ice Thickness (SIT) during 2012 and 2014

Stations 2012	SIT (m)	Stations 2014	SIT (m)
L1	1.62	D1	1.76
L2	1.59	D2	1.65
L3	1.46	D3	1.3
L4	1.58	D4	1.3
T1	1.29	D5	1.37
T2	1.45	D6	1.37
T3	1.57	D7	1.16
T4	1.62	D8	1.32
		D9	1.3

3.2 Variations at the ice water interface

During the 31-ISEA, entire Quilty bay region was characterized by hyperoxia (6.6–10.3 ml/L) when compared to ice free coastal Antarctic waters (5.2-5.3 ml/L), at C1 and C2 (Fig. 2). Ice drilled samples exhibited higher algal biomass, Chl a (0.6-6.1 mg/m³), whereas in the coastal Antarctic ice-free water at C1 and C2 the Chl a ranged between 0.4 and 0.5 mg/m³. The pCO₂ concentrations were <10 µatm in drilled samples and ranged from 287 to 301 µatm at C1 and C2 (Fig. 2). The sea ice cover acts as a barrier for exchange of climatically important gases like CO₂ and O₂ between the atmosphere and the sea. These CO₂ undersaturated waters under the ice cover had brownish mucilaginous aggregates comprising of tube forming diatoms, *B. adelienses* and *N. lecointei* (Fig. 3).

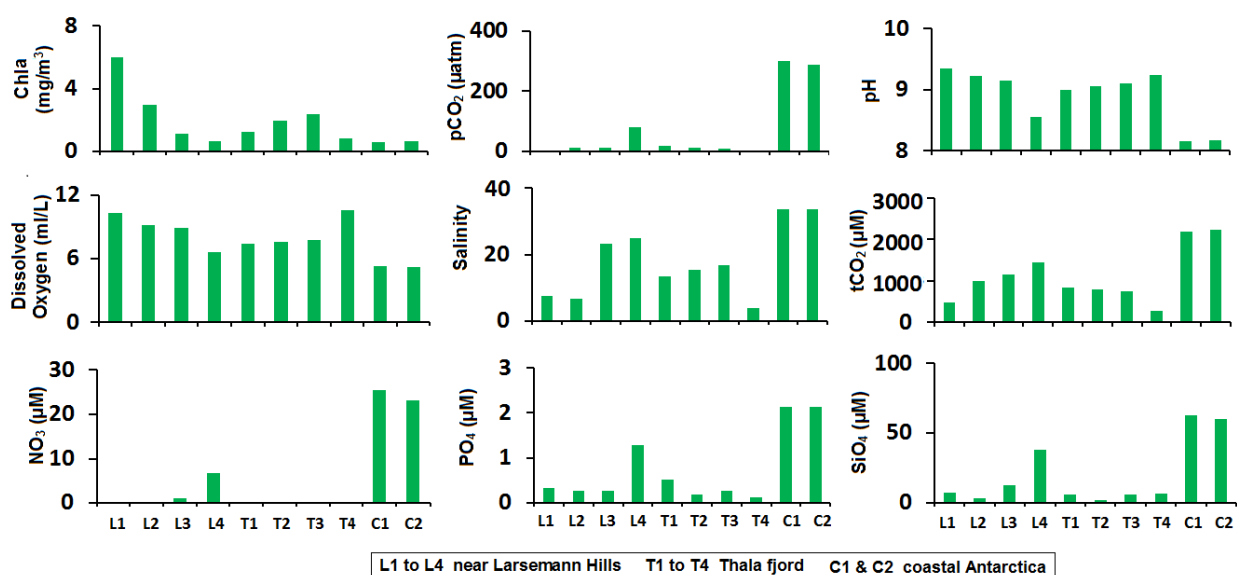


Figure 2: Variations in biogeochemical parameters at the ice water interface during 31-ISEA. L1 to L4 are samples from larsemann Hills, T1 to T4 are from Thala fjord and C1 and C2 representing ice free region.

The ice drilled samples exhibit a consistent low $t\text{CO}_2$ levels with a range of $545 \mu\text{M}$ (L1) - $1630 \mu\text{M}$ (L4) (Fig. 2). The pH values ranging between 8.5–9.3 highlight the low CO_2 concentration and an increase in the dissolved oxygen levels (10.3 mL/L). An increase in the nutrients (NO_3 , PO_4 and SiO_4) was observed and is associated with a rise in salinity towards the open oceanic waters. Concentrations of nutrients such as NO_3 ($0.04\text{--}6.7 \mu\text{M}$), PO_4 ($0.1\text{--}1.2 \mu\text{M}$) and SiO_4 ($2.7\text{--}37 \mu\text{M}$) beneath the sea ice were found to be low as compared to the coastal Antarctic waters, which had NO_3 ($16\text{--}25 \mu\text{M}$), PO_4 ($0.5\text{--}2.1 \mu\text{M}$) and SiO_4 ($40\text{--}62 \mu\text{M}$). Correspondingly, the Thala fjord exhibits low nutrient and Chl a concentration as we move towards the inner fjord with a corresponding decrease in salinity. The $t\text{CO}_2$ concentration was low towards the head of the fjord, having an ice thickness of 1.62 m, the concentration was $309 \mu\text{M}$ and $948 \mu\text{M}$ at the two extremes of fjord and pH ranged between 8.9 and 9.2. The surficial values during 31-ISEA (2011/12) and 33-ISEA (2013/14) showed that the oxygen and pH were slightly lower during the austral summer of 2014.

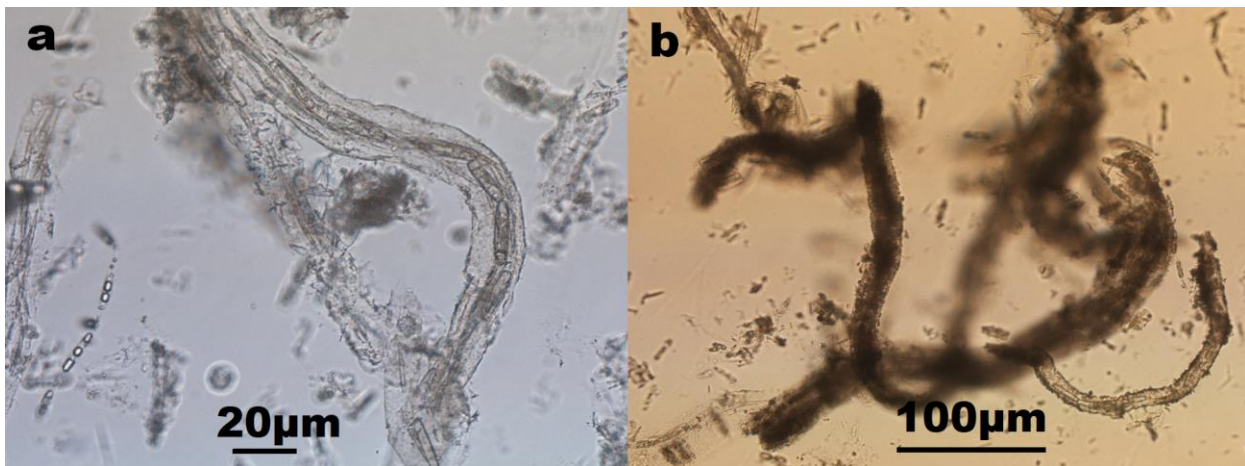


Figure 3: Light microscopic images of Tube forming diatoms and their tubes (a) *Berkeleya adelienses* and *Nitzschia lecointei* within the tubes (b) Tubes found attached to the under flanks of the sea ice.

As seen from Table 2, Chl a shows a moderate negative correlation with $p\text{CO}_2$ ($r = -0.41$) and salinity ($r = -0.44$), while Chl a has a moderate positive correlation with the dissolved oxygen ($r = 0.46$) and pH ($r = 0.58$). Dissolved oxygen and $p\text{CO}_2$ show a strong negative correlation ($r = -0.67$). Photosynthesis drives the production of dissolved oxygen and reduction in $p\text{CO}_2$. The negative correlation of Chl a and salinity indicates that the sea ice algae prefer lower salinities as compared to other open ocean phytoplankton groups. All the macronutrients (PO_4 , SiO_4 , and NO_3) showed weak

negative correlations with Chl a indicating rapid utilization and nutrient depleted conditions under the sea ice.

Table 2: Spearman rank correlation between various biogeochemical parameters.

	TCO₂	pH	PO₄	SiO₄	Chl a	Salinity	pCO₂	DO	NO₃
TCO₂	1								
pH	-0.74	1.00							
PO₄	0.71	-0.90	1.00						
SiO₄	0.68	-0.83	0.92	1.00					
Chl a	-0.34	0.58	-0.29	-0.36	1.00				
Salinity	0.82	-0.73	0.59	0.65	-0.44	1.00			
pCO₂	0.76	-0.95	0.97	0.94	-0.41	0.65	1.00		
DO	-0.70	0.84	-0.63	-0.46	0.46	-0.74	-0.67	1.00	
NO₃	0.68	-0.83	0.92	1.00	-0.36	0.65	0.94	-0.46	1.00

3.3 Variations at subsurface depths

The hyperoxic and low pCO₂ characteristics under the ice cover were observed only at the ice water interface and that the pCO₂ increased with depth with peak values at the bottom (Fig. 4). Simultaneously, a decrease in the dissolved oxygen concentrations was noticeable below the top few meters. The nutrient concentrations were found to increase considerably with depth. Temperature decreased from ice water interface (-0.3 °C) to the bottom (-2.2°C). Macro nutrients like SiO₄, PO₄ and NO₃ were as low as 0.5 μM, 0.06 μM, and 0.2 μM at the ice water interface and were 58 μM, 2.2 μM, and 43.6 μM, respectively at the bottom (160 m). Inorganic carbon (tCO₂) was depleted at the ice water interface (365 μM) as compared to the 160 m (2474 μM). Broadly, the vertical profiles demonstrate low pCO₂ and nutrients and high dissolved oxygen, pH and Chl a, only at the ice water interface.

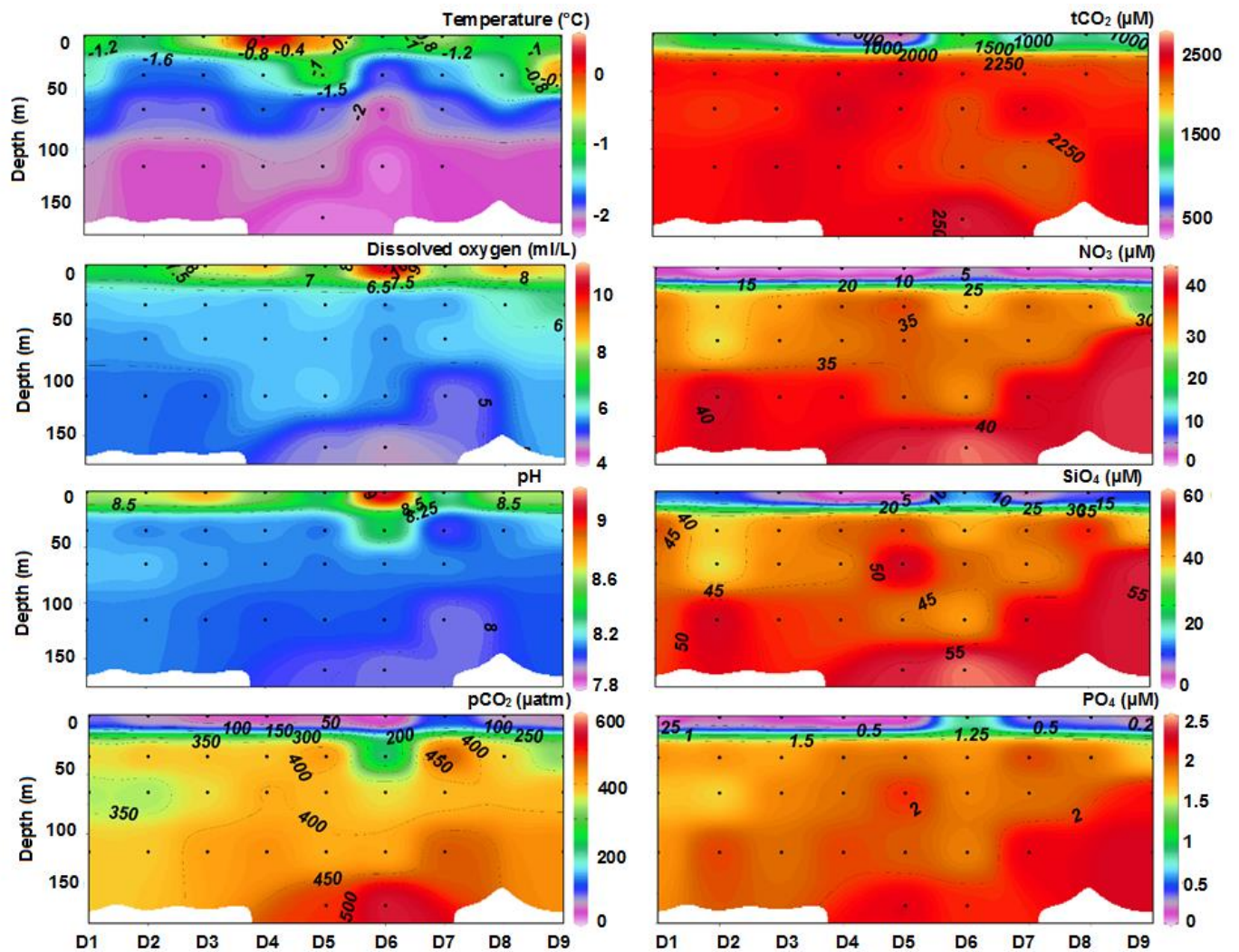


Figure 4: Vertical distribution of biogeochemical parameters beneath the ice cover collected during 2014.

4. Discussion

Exploring the biogeochemistry of the life existing in an environment at several meters of depth beneath the sea ice cover is fascinating and challenging. Our attempt in doing so revealed a unique ecosystem with life flourishing beneath the ice cover. We found sponges, their spicules, sea urchins, benthic diatoms and foraminifera thriving in these waters. Our results enhance our knowledge that the sea ice algae of the study area are well adapted to the low light, temperature and salinity conditions resulting in mucilaginous aggregates and high biomass. Sea ice cover acted as a barrier to the exchange of CO₂ between the atmosphere and the sea which lead to CO₂ under saturation and accumulation of dissolved oxygen beneath the ice. We report in this study the highest concentrations of dissolved oxygen for any aquatic ecosystem. Such hyperoxic oceanic regions are rare considering the recent reports of decline in global oceanic oxygen concentrations by more than 2% in last five

decades (Schmidtko et al., 2017). Apart from supplying oxygen to other oxygen depleted regions these under ice hyperoxic waters can also act as a strong CO₂ sink.

The observed CO₂ under saturation is biologically driven, as the pCO₂ changes are too large to result from temperature or salinity changes (Rubin et al., 1998) and are negatively correlated with Chl a concentration (Table 2). Besides being a barrier, the sea ice also acts as a protective cover by permitting only the requisite amount of light to penetrate through the sea ice, thereby inhibiting the harmful UV radiations from affecting the survival of under ice biota (Ishikawa et al., 2001; McMinn 1996; Odate et al., 2004). Light is considered as the main limitation to photosynthesis in fast ice bottom communities (Palmisano et al., 1985; Cota and Smith 1991; Smith et al., 1998). The sea ice algal communities are extremely shade adapted (Palmisano et al 1985; Palmisano et al., 1987; Irwin 1990; Lizotte and Sullivan 1991) as they increase their photosynthetic pigments under low light conditions (Falkowski and Raven 1997). This leads to an increase of accessory pigment like fucoxanthin, which is highly effective at absorbing wavelengths that can penetrate sea ice (Lizotte et al., 1998). Palmisano and Garrison (1993) even suggested that the sea-ice algae may be able to switch from autotrophy to heterotrophic uptake of organic matter.

As seen from table 2, nutrients show negative correlation with Chl a, indicating that the nutrient demand of sea ice algae under the ice cover is higher than its supply sources, leading to nutrient depleted conditions. In a need to overcome such conditions the *Berkeleya* species is suspected to live in symbiosis with other diatoms. The tiny pennate cells of *N. lecointei* were found to be living inside the tubes symbiotically with *B. adelienses*. From this study we can infer that inspite of stressed conditions of light and nutrient limitation, the photosynthetic activity of tube forming diatoms probably drives the pCO₂ concentration, resultant accumulation of dissolved oxygen, and an increase in pH beneath the ice-covered region. This capacity of tube forming diatoms could be attributed to its tube formation that results in better utilization of nutrients. Apart from nutrient depletion, the high biological activity makes the system devoid of inorganic carbon and thus the physiological differences in inorganic carbon uptake may control species diversity of sea ice algae (Thomas and Dieckmann 2002).

The sea ice thickness during January 2012 (1.52 m) was greater than during January 2014 (1.39 m). The build-up of oxygen was thus higher during 2012 as compared to 2014. Even Chl a was higher during 2012 (6.1 mg/m³) as compared to 2014 (1.4 mg/m³). This environment under the sea ice is prone to many chemical changes, which includes hyperoxia, CO₂ undersaturation, highly alkaline pH, and nutrient depletion due to restricted sea-air exchange and mucilaginous aggregates of tube forming diatoms. Thomas and Dieckmann (2002) reported pH values as high as 11 within the sea ice

brines. In such highly oxic conditions, there is a possibility that toxic photochemical products, including hydrogen peroxide and hydroxyl radicals, may get accumulated (Vincent and Roy 1993; Prézelin et al., 1998). McMinn et al. (2000) reported oxygen bubbles at the ice water interface and concluded that it could have contribute to the demise of algal bloom. Under such stressful conditions, diatoms flourish by negating hyperoxia using anti-oxidative enzymes (Raven 1991; Raven et al., 1994; Rijstenbil 2001).

This investigation documents mucilaginous aggregates of tube forming diatoms under the thick sea ice cover in the Quilty bay. Recent studies have reported an increase in Antarctic Sea ice extent and thickness (Williams et al., 2015; Meehl and Teng 2016), however in last few years Antarctica has recorded the lowest Sea ice extent (NSIDC 2019). Loss in sea ice cover would decrease the frequency of under ice phytoplankton blooms. Sea ice melting would therefore add nutrients to the water column and could change the nutrient ratios. The changes in sea ice volume and/or extent can alter the nutrient cycling and the seasonal timing of nutrient availability to phytoplankton (Wang et al., 2014). Sea ice melting would also decrease the salinity and could lead to phytoplankton community shift with an important consequences for the Antarctic food web and coastal biogeochemistry. In the Antarctic coastal region, Mendes et al. (2013) reported transition from a system traditionally dominated by diatoms to one dominated by cryptophytes due to decrease salinities resulting from glacial melting.

Sea ice extent can affect krill abundance and seriously alter Antarctic food web structure (Flores et al., 2012). Processes like ocean acidification which are reported in the Southern Ocean (Orr et al., 2005), might reduce the light utilization efficiency of the Antarctic diatoms (Hoppe et al., 2015). Our earlier studies have highlighted rapid transition in biogeochemical processes and CO₂ sink capacity in the Southern Ocean during transition from austral summer to early winter (Shetye et al., 2015). Shetye et al. (2017) reported the dual nature of sea ice in biogeochemical processes, while Shetye et al. (2014) reported the rapid depletion in SiO₄ under the Antarctic sea ice. Our future studies will focus on the under-ice biogeochemistry during winter, as the high biomass generated during summer and the thick fast ice cover might result in acidic or anoxic conditions during winter.

5. Conclusions:

From the overall view of the biogeochemical parameters that were measured, it is concluded that there is a severe depletion in pCO₂ at the ice water interface, associated with hyperoxia and mucilaginous aggregates of tube forming diatoms. It is implied that the photosynthetic activity of the phytoplankton shows a maxima at the surface and decreases as the depth increases. Immediately

beneath the ice there is an abrupt increase in the nutrient concentration along with the $t\text{CO}_2$ concentration with a succeeding decrease in the pH and dissolved oxygen concentration. Intensive studies are required on the adaptations of sea ice algae towards CO_2 limitation and hyperoxia during summer. The recent changes in Antarctic sea ice extent and concentration may negatively affect the under ice phytoplankton blooms. The melting of ice will also increase the nutrient supply from the land via streams and glaciers and will result in community shifts.

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