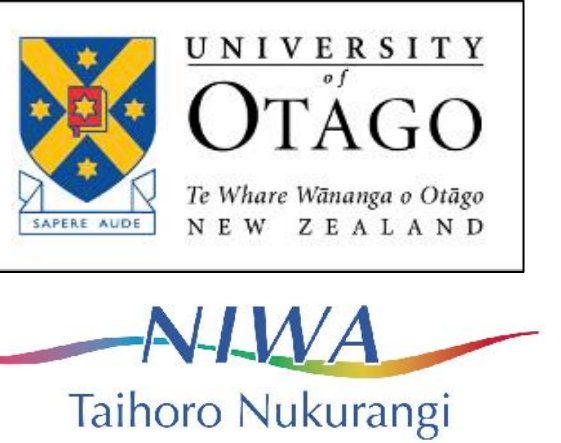


Quantifying the Carbonate Chemistry and pH Variations of Otago Harbour, New Zealand

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Methods

Satlantic SeaFET

- Continuous deployment (42 days, Fig.1 Site C)
- Burst ISFET pH readings every 30 minutes at surface (depth 1m)

YSI 6600 Sonde

- Weekly measurement of *in situ* seawater characteristics (Fig.1 Sites A & B, at ≈0.1m depth & B at ≈0.5m depth)
- Measures temp (°C), salinity, dissolved oxygen (DO, mg/L) and chlorophyll-*a* concentration (µg/L)

Horiba U51

- Alternative to the Sonde; *in situ* seawater measurements (Fig.1 Sites A & B)

Water Samples

- Weekly intertidal and subtidal samples (Fig.1 Sites A & B, ≈0.1m and ≈0.5m respectively)
- From Mar – Oct 2015
- Dissolved Inorganic Carbon (DIC) and Total Alkalinity (TA) processed post collection
- pH, pCO₂, Ω_c and Ω_a were calculated in the program CO₂calc (Hunter 2009)

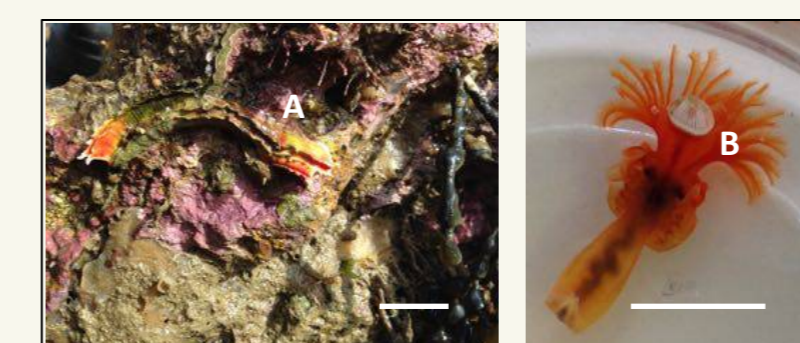


Introduction

Ocean Acidification (OA) is altering carbonate chemistry by reducing seawater pH, increasing pCO₂, and causing under-saturation of Ω_c and Ω_a. Extensive research has been conducted to project future OA conditions based on offshore datasets and global open ocean averages (IPCC 2007, 2013). However, **biological and ecological complexities of coastal zones make it difficult to accurately predict the response of these systems to OA.** Carbonate chemistry parameters and pH fluctuations are ecosystem specific and vary based on local conditions (Hofmann et al. 2011). In order to design meaningful *in vitro* experiments that test biological responses to OA, **site-specific carbonate chemistry parameters and pH variations can be used to develop ecologically relevant pH targets.**

Aims

To create a **baseline understanding of carbonate chemistry parameters and pH variation in a coastal zone of Otago Harbour** at a location where my study species, the tubeworm *Galeolaria hystrix* (Box 1), occurs. To more accurately **understand this species' current pH exposure** so subsequent experiments can be **designed to test ecologically relevant pH levels** for biofilm development and settlement assays. For more information see my presentation "**Biofilms: Are they the missing link in understanding the effect of OA on settlement selection?**" May 6th at 2:45pm, GB 3.

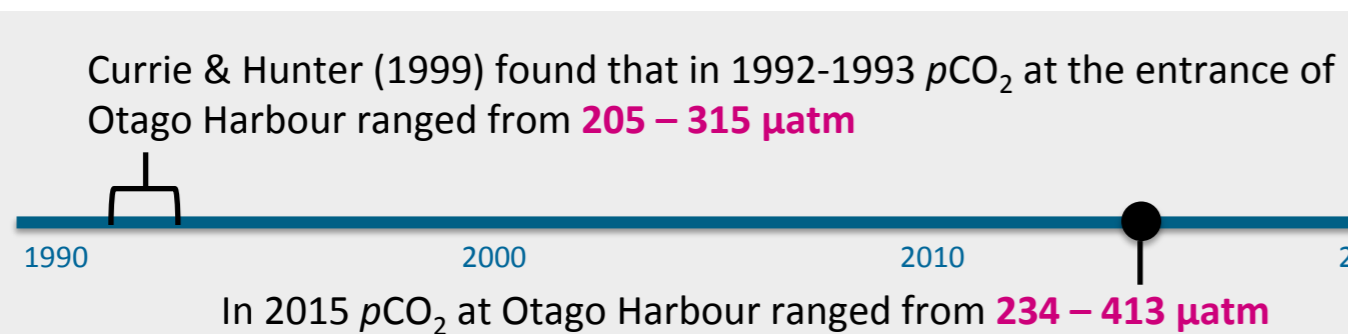


Box 1: *Galeolaria hystrix*
Adult *Galeolaria hystrix* Mörch 1863 (Polychaeta: Sebellida, Serpulidae) is a relatively large tubeworm with a distinctive red/orange calcareous tube (A) and brachial crown (B) that is found in the low intertidal and subtidal zones of New Zealand and Australia. Scale bar represents 1cm.

Results

Summary & Key Conclusions

Annual Average pH_T = 8.13 ± 0.01
Seasonal, diurnal and semi-diel fluctuations in pH_T were moderate (≈ 0.02 ≤ pH_T ≤ 0.11)



Seawater pH_T Variations

- Primary Frequency** = Diurnal increases in pH_T correspond to light (PAR),
- Secondary Frequency** = Smaller peaks and troughs correspond to tidal height (m) and occur at low and high tide respectively.

Findings suggest that **mixed algae assemblages and phytoplankton productivity help to buffer seawater pH_T** in light conditions and **tidal fluctuations bringing off-shore water in and out of the harbour** are primarily responsible for the observed natural variations in pH_T.

Carbonate Chemistry Parameters

- Seasonal shifts in carbonate chemistry **correspond to seasonal shifts in seawater characteristics** such as temperature (°C), chl-*a* (µg/L) and Beaufort wind force.
- Disruptive weather activity and higher Beaufort wind forces** over winter may have **increased freshwater input and mixing**, stimulating primary production and causing the observed **"net biological DIC decreases" and associated shifts in carbonate chemistry** (Ingrosso et al. 2016).
- Findings highlight the **importance of the frequency and intensity of storm events, runoff, currents, tides and mixing** in determining the carbonate system and patterns of variability on the local scale.

Ecologically Relevant pH Targets

The average pH_T was reasonably consistent with the **2010 global open ocean average of pH_T 8.07** and variations were moderate. Due to these findings, pH targets based on IPCC projections (2007, 2013) for subsequent experiments were verified: **pH 7.8 (2100, near-future) and pH 7.4 (2300, extreme).**

Seawater pH_T Variations

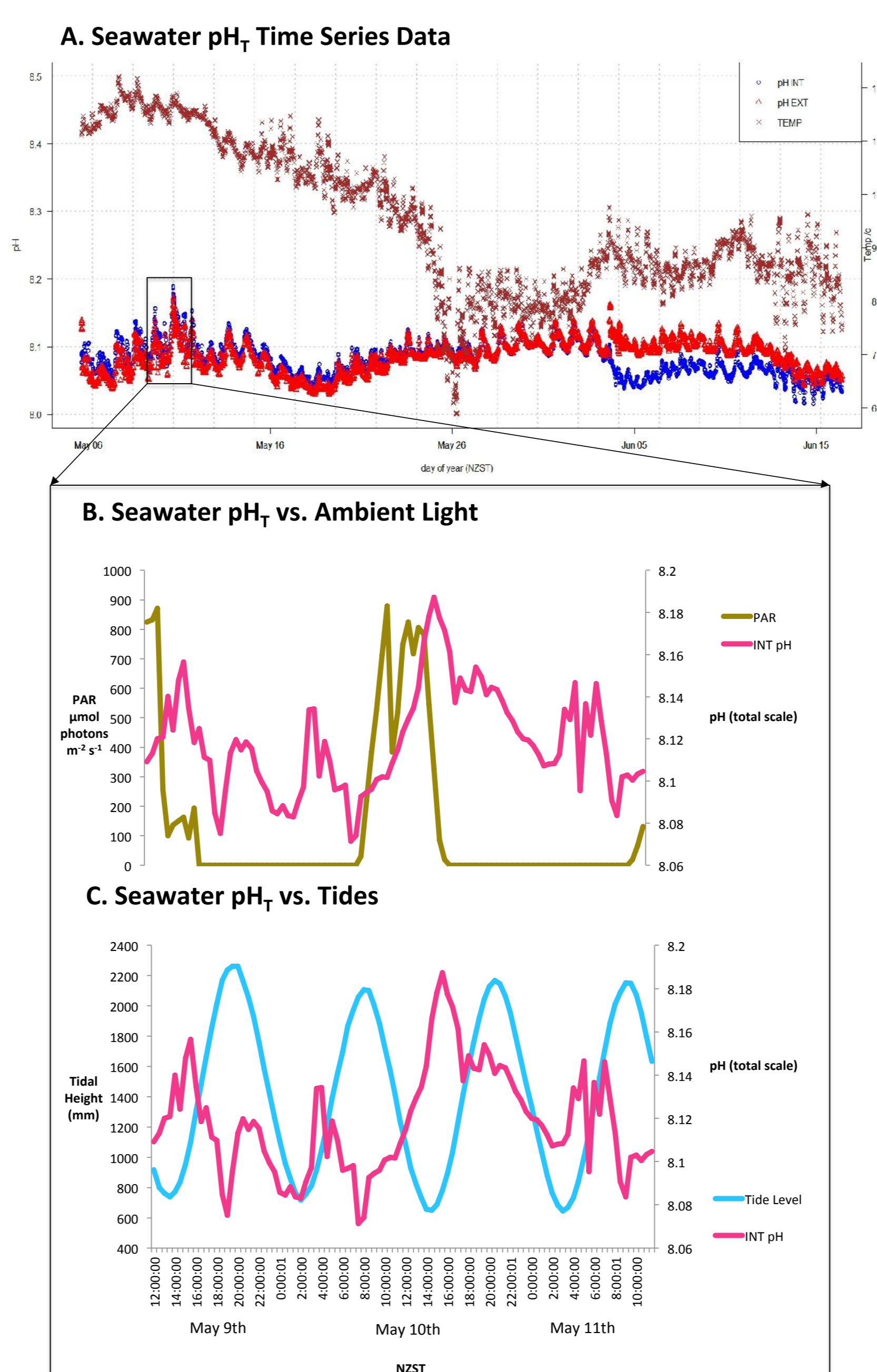


Figure 4. (A) Long term dataset from the 42-day deployment of the SeaFET at Site C (Fig. 1) from 5 May - 16 June 2015. (B) Compares SeaFET pH_T data to PAR (photosynthetically active radiation, 700-400nm) light data collected at Portobello Marine Lab from 9 - 11 May, 2015. (C) Compares SeaFET pH_T data to tidal height (m) data collected at Portobello Marine Lab from 9 - 11 May, 2015.

Carbonate Chemistry

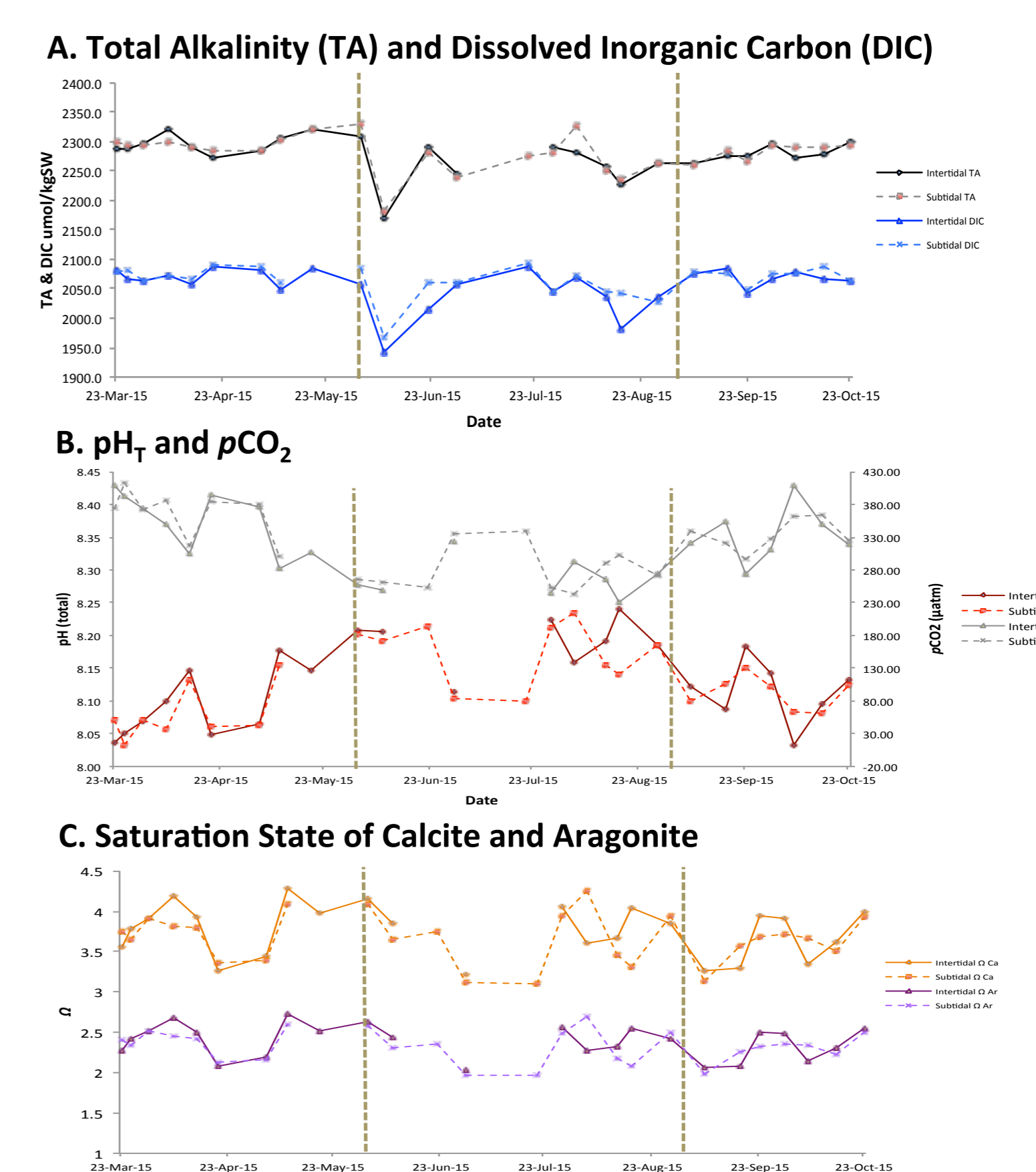


Figure 5. (A) TA and DIC measurements from Sites A & B (Fig. 1). (B) Calculated pH_T and pCO₂ at Sites A & B (Fig. 1). (C) Calculated saturation states of calcite (Ω_c) and aragonite (Ω_a) at Sites A & B (Fig. 1). All graphs (A-C) show results from March to October 2015. Vertical dotted lines represent the delineation between seasons. Data collected in March-May 2015 is defined as "autumn", June-August is defined as "winter" and September-October is defined as "spring".

Table 1. Summary of key seawater averages annually and over seasons. Annual averages represent all data collected from March – October 2015. Data collected in March – May 2015 is defined as "Autumn", June – August 2015 is defined as "Winter" and September-October is defined as "Spring". Numbers in brackets () equate to ± one standard error.

	Annual Average	Autumn Average	Winter Average	Spring Average
Temp (°C)				
Intertidal	10.28 (0.53)	12.81 (0.62)	7.81 (0.33)	10.55 (0.75)
Subtidal	10.10 (0.52)	12.63 (0.62)	7.63(0.30)	10.39 (0.69)
Salinity (ppt)				
Intertidal	33.75 (0.15)	34.20 (0.16)	33.37 (0.34)	33.64 (0.09)
Subtidal	33.79 (0.15)	34.29 (0.18)	33.43 (0.29)	33.65 (0.08)
DO (mg/L)				
Intertidal	8.67 (0.39)	8.25 (0.34)	9.02 (0.95)	8.72 (0.36)
Subtidal	8.39 (0.31)	7.85 (0.25)	8.57 (0.95)	8.83 (0.32)
Chl-<i>a</i> (µg/L)				
Intertidal	2.4 (0.2)	2.0 (0.2)	3.2 (0.5)	2.2 (0.2)
Subtidal	2.3 (0.3)	1.6 (0.1)	3.4 (0.6)	2.1 (0.2)
Beaufort Wind Force	2.12 (0.27)	2.22 (0.32)	2.8 (0.45)	1.64 (0.61)
TA (µmol/kgSW)				
Intertidal	2278.5 (6.3)	2296.6 (5.4)	2259.0 (14.0)	2280.5 (5.0)
Subtidal	2281.6 (6.0)	2297.1 (3.6)	2266.7 (13.7)	2283.1 (5.2)
DIC (µmol/kgSW)				
Intertidal	2056.2 (6.6)	2072.2 (4.5)	2033.3 (13.7)	2068.1 (5.3)
Subtidal	2064.4 (5.2)	2075.8 (3.9)	2049.8 (11.1)	2072.4 (4.7)
pH (total)				
Intertidal	8.13 (0.01)	8.09 (0.02)	8.19 (0.01)	8.11 (0.02)
Subtidal	8.13 (0.01)	8.08 (0.01)	8.17 (0.01)	8.11 (0.01)
pCO₂ (µatm)				
Intertidal	313.09 (12.36)	354.32 (15.35)	267.44(10.47)	333.76 (16.14)
Subtidal	323.14 (9.69)	365.77 (13.38)	281.71 (10.83)	333.61 (8.82)
Ω_c				
Intertidal	3.80 (0.08)	3.81 (0.11)	3.80 (0.11)	3.62 (0.12)
Subtidal	3.66 (0.06)	3.72 (0.09)	3.66 (0.13)	3.60 (0.09)
Ω_a				
Intertidal	2.41 (0.05)	2.44 (0.07)	2.40 (0.07)	2.30 (0.08)
Subtidal	2.33 (0.04)	2.38 (0.06)	2.31 (0.08)	2.29 (0.06)

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