Testing the fidelity of global biogeochemical algorithms in the California Current System to study carbon cycling

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Abstract

Ocean acidification (OA) is the result of increasing anthropogenic carbon in the atmosphere that leads to increasing anthropogenic carbon in the ocean, thereby triggering a decrease in seawater pH (Doney et al., 2009; Waldbusser et al., 2014). As carbon dioxide gas (CO_2) increases in the atmosphere and dissolves into the ocean, near surface ocean pH values decline thus shifting the carbonate equilibria and decreasing the saturation state of carbonate minerals (Cyronak et al., 2015). These shifts in seawater chemistry can disrupt the ability of calcifying organisms to maintain shells made of calcium carbonate. The saturation state of aragonite (Ω_{arag}) is a parameter used to describe the stability of the aragonite mineral phase of $CaCO_3$ in the environment. Chemically, calcium carbonate dissolution is favored when $\Omega_{arag} < 1$ while precipitation is favored when $\Omega_{arag} \geq 1$; however, marine organisms can work to regulate the production of $CaCO_3$ minerals by modifying internal calcification fluids. Recently, the substrate-to-inhibitor ratio (SIR), or the ratio of bicarbonate (HCO_3^-) to hydrogen ions (H^+), has been proposed as an alternative metric to estimate the biological calcification potential of marine creatures (Bach et al., 2015; Fassbender et al., 2016). While debate remains about which metric (Ω_{arag} or SIR) is more meaningful for interpreting impacts on biological calcification, the purpose of this study is to first evaluate the fidelity of open ocean algorithms in order to apply them to glider observations in the California Current System for OA research. Glider data provided by the Central and Northern California Ocean Observing System (CeNCOOS) were analyzed using MATLAB software to evaluate variabiltiy in the Ω_{arag} and SIR relationship in a region of extensive upwelling and active shellfish aquaculture. These

preliminary results provide insights about the exposure of calcifying organisms, particularly those in the benthos, to ocean acidification now as well as during the preindustrial era.

Introduction

The California Current System

Eastern Boundary Current systems (EBCs) are some of the most biologically productive in the world but they are also particularly sensitive to climate change (Bakun et al., 2015). The California Current System (CCS) is an EBC with waters sourced from the North Pacific Current as well as the California Undercurrent off Baja California, Mexico (Checkley et al., 2009). Seasonal upwelling occurs annually between May and October powered by strong Northwestern winds. These winds drive surface waters offshore due to the curve of the Earth (i.e., Coriolis effect) thereby allowing cold, deep, nutrient rich water to fill the void, often breaching the surface (Figure 1a) (Summerhayes et al., 1985; Barton et al. 2015; Kudela et al., 2008). Upwelled waters are the dominant source of nutrients in Eastern Boundary Current systems, supporting higher dynamic trophic levels (Kadula et al., 2008 & Todd et al., 2018). This upwelling process (Figure 1b) is evident along the United States West Coast with lower sea surface temperature and higher chlorophyll concentrations found along the coastline (Chavez, et al. 1991, Feely et al., 2008; Hutchings et al., 1985). The high chlorophyll concentrations acts as a proxy for phytoplankton biomass, which demonstrates the high productivity fueled by the upwelled nutrient supply supporting a wide range of trophic levels including commercial fisheries (Kadula et al., 2008; Bakun et al., 2015).

The CCS in particular is an important region for fisheries and commercial shellfish nurseries. However, these fisheries are threatened by the rise in atmospheric carbon dioxide (CO_2) largely due to carbon emissions from anthropogenic activities (Doney et al., 2009; Waldbusser et al., 2014). The associated changes in seawater chemistry (i.e., OA) are causing large scale biogeochemical shifts including decreases in ocean surface pH, carbonate ion concentrations, and carbonate saturation states (Orr et al., 2005).

Studying how OA is impacting coastal regions, like the CCS, can be challenging due to the sporadic nature of upwelling events coupled with riverine input and human influences near shore (i.e., pollution)(Fassbender et al., 2016). Ship based observations provide high quality data and can reveal large-scale patterns. However, their observing coverage is often limited in time and space due to the expense and safety concerns associated with weather conditions. On the other hand, autonomous vehicles, such as underwater gliders, can collect observations on finer spatial scales and over longer time periods (Chai et al., 2012;Rudnick, 2015). In this preliminary study both cruise and glider data were processed and interpreted. Although the OA relevant metrics (Ω_{arag} or SIR) cannot be measured directly, they can be estimated from observations of other parameters.

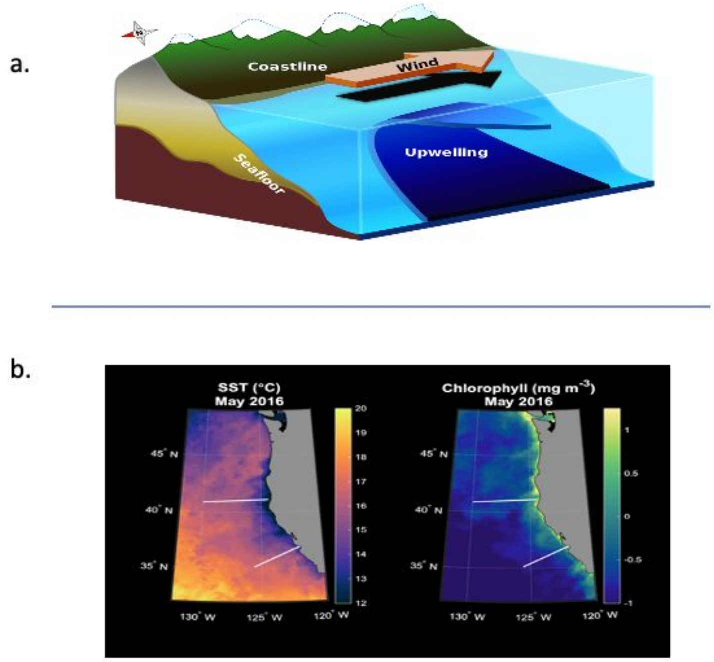

Figure 1. The process of upwelling is a dominant feature of the California Current System (a). The result of upwelling is often lower sea surface temperature (SST) and higher chlorophyll-a concentrations near shore (b).

OA metics: Ω_{arag} and SIR

When CO_2 dissolves into the seawater it reacts with water to form carbonic acid (H_2CO_3). Carbonic acid often loses a hydrogen ion to form bicarbonate ($[HCO_3^-]$), which is often taken up by calcifying organisms that make shells or plates from calcium carbonate ($CaCO_3$) (Raven et al., 2005). Inside the organism, this molecule loses another proton to form a carbonate ion ($[CO_3^{2-}]$) and when used with a calcium ion ($[Ca^{2+}]$) can form calcium carbonate shells. The CCS is expected to experience the negative impacts of OA sooner than other regions in the ocean due the upwelling process bringing old deep CO_2 rich waters to the sea surface. In addition the upwelling process will also bring deep corrosive and undersaturated waters to the surface (Alin et al., 2012; Chhak & Di Lorenzo, 2007; Feely, 2008). The aragonite saturation state (Ω_{arag}) is the measure of the thermodynamic favorability of precipitation of the mineral phase.

$$\Omega_{arag} = \frac{[Ca^{2+}][CO_3^{2-}]}{K'_{sp}}$$

Ω_{arag} is a useful proxy for determining the temporal and spatial variability of a carbonate system as well as how organisms may respond towards it. K_{sp} is the solubility product of the specified $CaCO_3$ mineral phase, aragonite or calcite, where aragonite is considered more soluble than calcite (Zeebe & Wolf-Gladrow, 2001;Cyronak et al., 2015; Fassbender et al., 2016). When the Ω_{arag} is equal to one it is in equilibrium with the surrounding seawater. $CaCO_3$ precipitation, or the process of the shell formation, is chemically favored when $\Omega_{arag} \geq 1$. While, $\Omega_{arag} < 1$ dissolution of $CaCO_3$ is favored (Morse & Rolf, 2002;Cyronak et al., 2015). [Ca^{2+}] is largely a function of salinity, which doesn't change much in the ocean. Therefore, the stability of aragonite or calcite mineral phases is largely dependent on the [CO_3^{2-}] concentration. Decreasing seawater pH and [CO_3^{2-}] with OA will make it more difficult for calcifying organisms to maintain their shell (Bach et al., 2015). However, Ω_{arag} is not the only metric used to estimate calcification potential. The substrate-to-inhibitor ratio, or SIR is the ratio of bicarbonate ion ([HCO_3^-]) to Hydrogen ion ([H^+]).

$$SIR = \frac{[HCO_3^-]}{[H^+]}$$

After acquiring [HCO_3^-] from seawater, the calcification process within an organism requires converting [HCO_3^-] to [CO_3^{2-}], which causes an increase in the internal hydrogen ion concentration. The organism must then expel [H^+] to maintain constant internal pH (Taylor et al., 2011;Mackinder et al., 2015; Bachet al., 2015). The decrease in seawater pH is associated with an increase in the [H^+], making it more difficult for organisms to expel internal [H^+]. Increased SIR values suggest favorable conditions for calcification while lower values are indicators of unfavorable conditions (Jokiel, 2011; Fassbender et al., 2016).

Both SIR and Ω_{arag} are metrics for possibly determining the chemical favorability of $CaCO_3$ precipitation or dissolution. Evaluating these two different parameters along the United States West Coast is of extreme importance because the CCS is a hot spot for shellfish nurseries and benthic vertebrates which are directly affected by OA conditions (Fabry et al., 2008). The California Current Systems coastal upwelling has previously been shown to bring low SIR values and Ω_{arag} levels less than one to the surface near shore (Feely et al., 2008; Kudela et al., 2008; Cai et al., 2020).

The fundamental purpose of this preliminary study is to first evaluate the fidelity of open ocean algorithms in order to apply them to glider observations in the California Current System for OA research. Glider data supplied by CeNCOOS were analyzed using MATLAB software to evaluate variabiltiy in the Ω_{arag} and SIR in a region of extensive upwelling and shellfish nurseries.

Methods

In this preliminary study the performance of open ocean algorithms were tested in order to assess their potential for application on autonomous underwater gliders for carbon cycle research. The fidelity of the open ocean algorithms were tested on high-quality West Coast Ocean Acidification (WCOA) cruise data collected between 2007 and 2016. The first algorithm is the CArbonate system and Nutrients concentration from hYdrological properties and Oxygen using a Bayesian Neural-network (CANYON-B). CANYON-B was used to estimate relevant nutrient variables, like nitrate, phosphate, silicate, in addition to important carbonate system parameters including dissolved inorganic temperature (DIC), total alkalinity (TA) , pH, and pCO_2. In addition, the algorithm provides a local 95% confidence interval for each estimated value (Sauzède et al., 2017;Bittig et al., 2018). The second algorithm of interest, the Linear Interpolated Regression (LIR) equations, computed values based on a linear regression model

(Carter et al., 2016). These two open ocean algorithms were based on the Global Ocean Data Analysis Project version 2 (GLODAPv2), which is a quality controlled dataset for ocean biogeochemistry (Bittig et al., 2018).

These algorithms were applied and their performance was evaluated for the WCOA cruises for 2011 to 2013 using MATLAB R2020a software. There were two prominent ways to assess the accuracy of the algorithms. The first was a qualitative plot of the parameters involved in the calculation of SIR and Ω_{arag}, particularly DIC, pH, and silicate. The values calculated from CANYON-B were plotted against the measured values to visualize whether there is a general agreement between the two. The more rigorous method used to assess both of the algorithm's performance for calculating DIC, pH, and silicate included plotting the biases of these variables at depth.

In order to make sure that these algorithms would also perform well when applied to glider data, it had to be determined that the glider data were of sufficient quality. There were two different types of glider data that was accessed from the Central & Northern California Ocean Observing System (CENCOOS). The SPRAY glider CalCOFI line 66.7 and 67, in addition to the Trinidad Head Line (THL) were evaluated in order to determine what transects had prominent upwelling (Rudnick, 2016; Rudnick et al., 2017). The transect of interest was a THL glider transect that occurred between May and June of 2019. The THL transect and the most recent cruise data from 2016 were plotted against the potential density anomaly (sigmaθ) which acts analog to depth.

The variabiltiy of the Ω_{arag} and SIR of the particular THL transect demonstrating upwelling was viewed from 100 kilometers from shore and 350 decibars at depth. The Ω_{arag} and SIR were calculated from the high quality cruise data to show a general agreement between the calculated values from glider data and the cruise data. The same calculations used to calculate the Ω_{arag} and SIR were repeated after removing the estimated anthropogenic carbon burden, allowing for evaluation of Ω_{arag} and SIR before the industrial revolution. The difference between pre-industrial values and current values were also calculated in order to visually understand where the largest difference has occurred.

The monthly seasonal variability of Ω_{arag} and SIR was analyzed using multiple glider lines from the THL over a 4-year period. The monthly average and standard deviation of SIR and Ω_{arag} were calculated at 35 kilometers from shore between 100- 200 meters in the water column and in the upper 20 meters of the column.

Results

Evaluation of Algorithm Performance

Assessment of the algorithm's performance on the WCOA cruise observations does not include the observations from 2007 and 2016 because they were included in the original algorithm training dataset. The first way to evaluate the performance of the CANYON-B algorithm demonstrated that the data falls along the one to one line generally well showing an agreement between the observed and calculated values (Figure 2a). The more robust analysis displays that both LIR's and CANYON-B average biases fall within the algorithm's given the 95% confidence intervals (Figure 2b). However, CANYON-B performs slightly better with nutrients particularly silicate, therefore CANYON-B will be applied to glider data to analyse OA metrics.

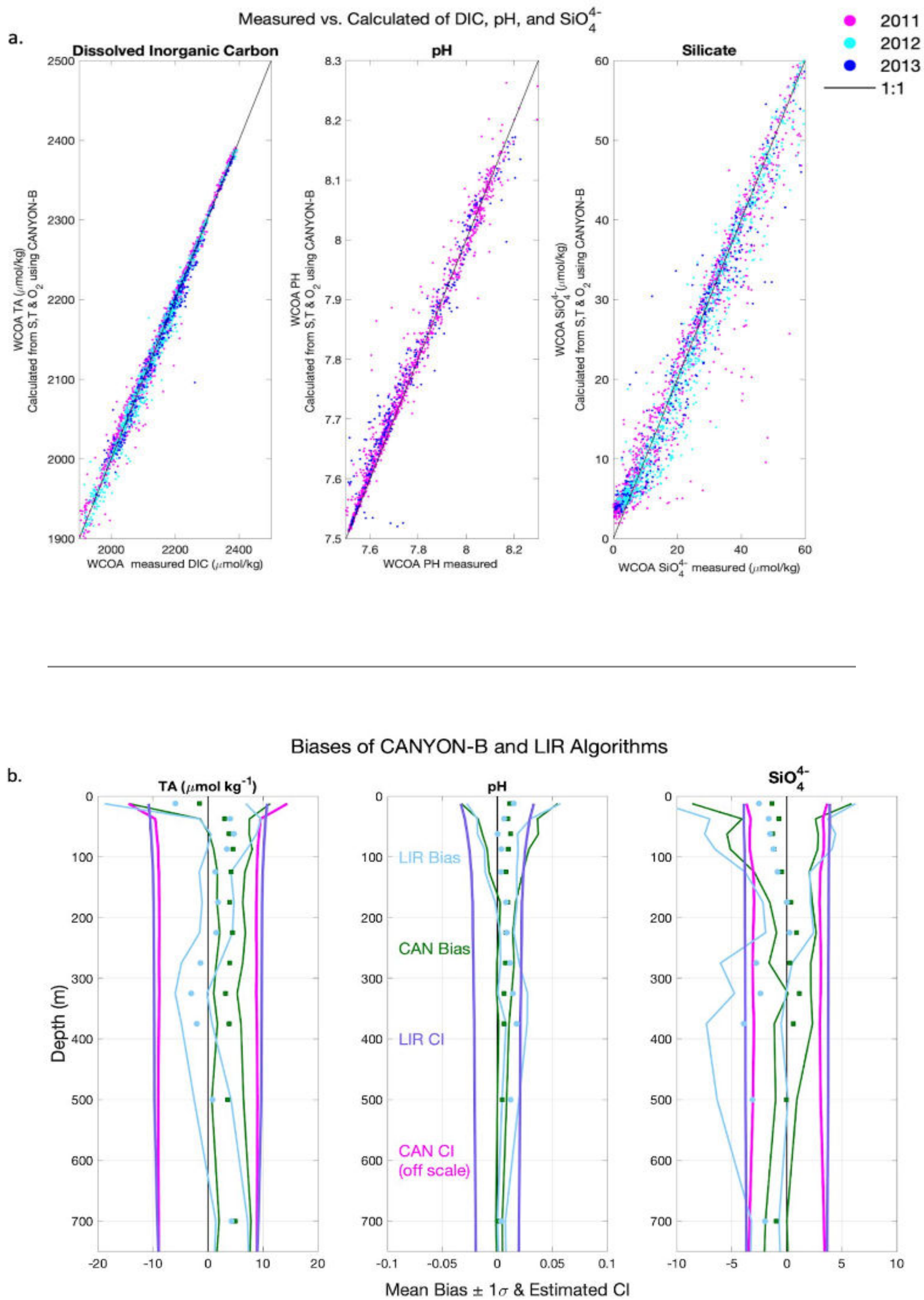

Figure 2. Assessment of the performance of open ocean algorithms (a) qualitative analysis shows the calculated values versus the measured values of dissolved inorganic carbon, pH, and silicate. (b) A more robust analysis of these variables biases plotted by depth.

Evaluation of Glider Quality

The THL glider transect from 2019 and the WCOA cruise from 2016 can be truly compared because the glider transect of interest is in close proximity to the most recent WCOA cruise from 2016 (Figure 3a). Furthermore, the oxygen, salinity, and temperature data from the glider transect and the cruise overlap nicely at depth (Figure 3b). The overlap of the THL transect data and cruise data indicates that applying CANYON-B in this preliminary study will yield trustful results.

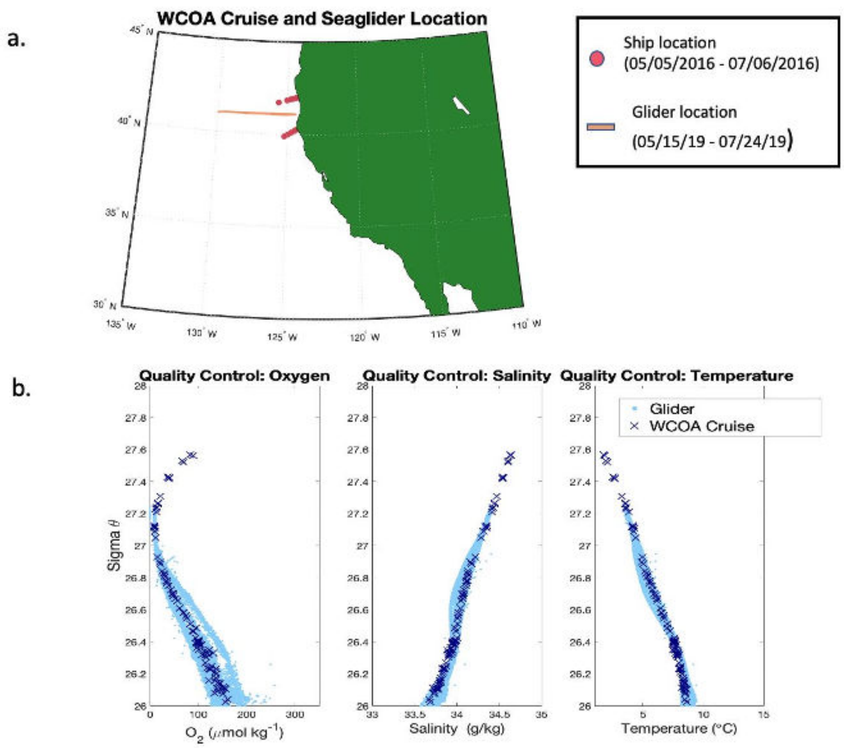

Figure 3. Quality control of glider data from 2019 (a) map of position of the glider and high quality ship data (b) cruise data plotted on top of glider data showing a general agreement at depth.

Evaluation SIR and Ω_{arag}

Upwelling that brings deep cold, nutrient rich water to the sea surface from will also bring lower Ω_{arag} values at depth to the sea surface (Feely et al., 2017). The upwelling event in Figure 4 demonstrates that Ω_{arag} values below one are bathing the continental shelf. However, the pre-industrial values show a much less extreme environment, where there is less corrosive waters washing the shelf. The difference between the current Ω_{arag} and pre-industrial Ω_{arag} values were greatest at surface waters.

The substrate-to-inhibitor ratio was also evaluated during this upwelling event. Similar to current Ω_{arag} the deep water is characterized by low SIR values that are being upwelling onto the continental shelf

(Figure 5). Pre-industrial SIR also had higher values displaying more favorable conditions. Furthermore, the largest difference between current and pre-industrial SIR was at the surface.

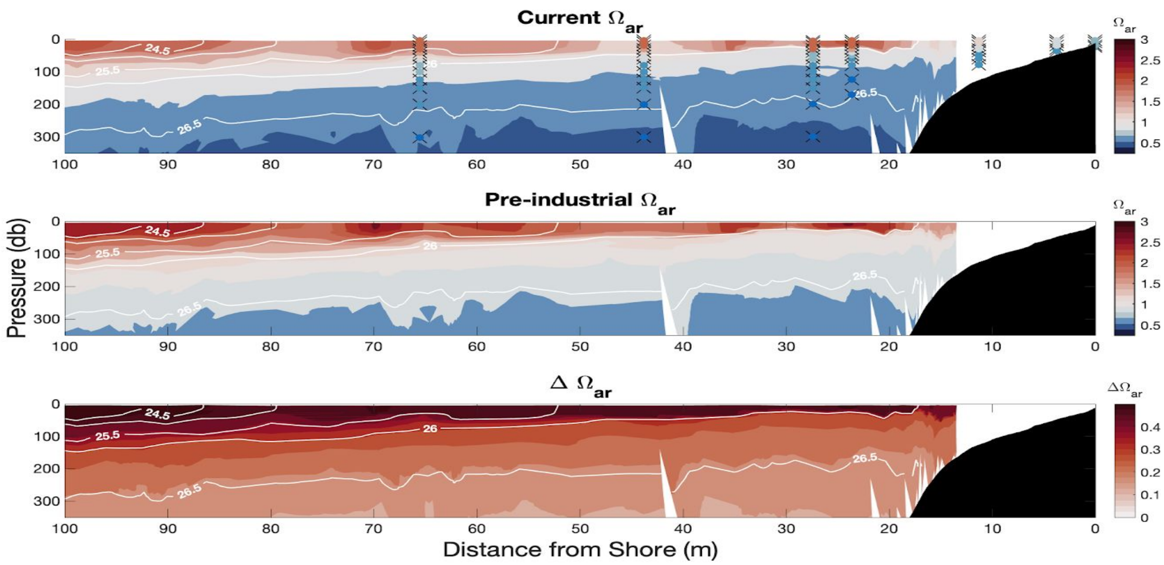

Figure 4. Upwelling event of THL transect between May and June of 2019. The top panel displays modern values of Ω_{arag} with overlaid cruise values. Values below one, indicated in white on the colorbar, demonstrate corrosive conditions. The middle panel shows less corrosive conditions in pre-industrial times. The last panel is the difference between pre-industrial values and current values.

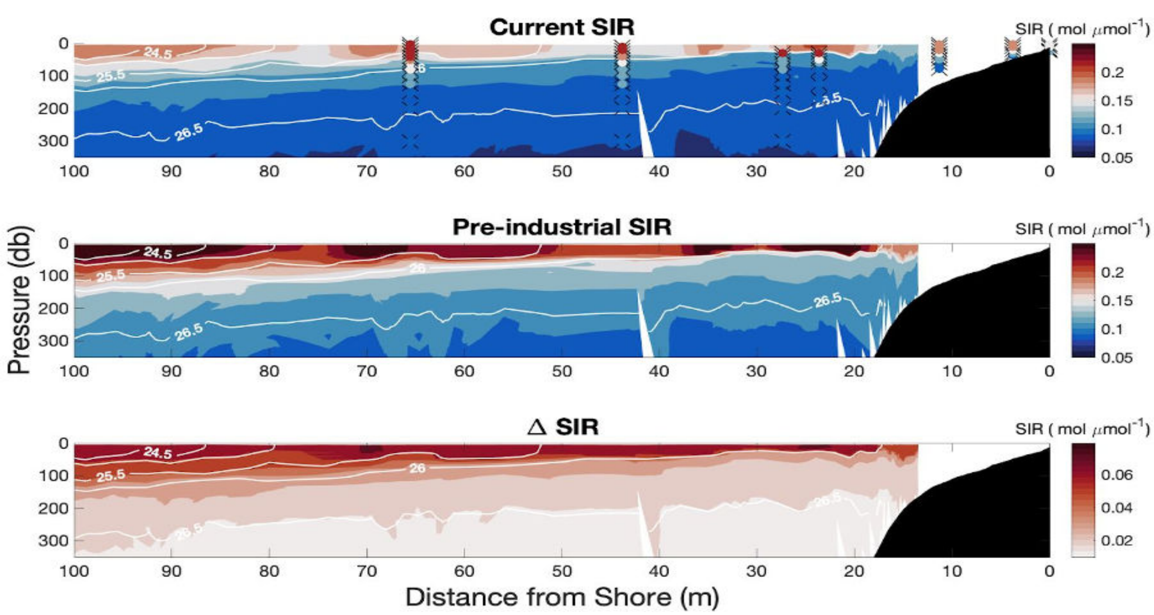

Figure 5. Upwelling event of THL transect between May and June of 2019. The top panel displays modern values of SIR with overlaid cruise values. Lower SIR values that are less favorable for calcification are upwelled onto the shelf.. The middle panel shows less extreme conditions in pre-industrial times. The last panel is the difference between pre-industrial values and current values.

Seasonal Variability of Glider data

In order to understand the seasonal variability of Ω_{arag} and SIR the average monthly values of these metrics were calculated in the upper 20 meters and between 100-200 meters of the water column. There was lower SIR and Ω_{arag} at depth compared to the values calculated in the upper 20 meters of the water column (Figure 6).

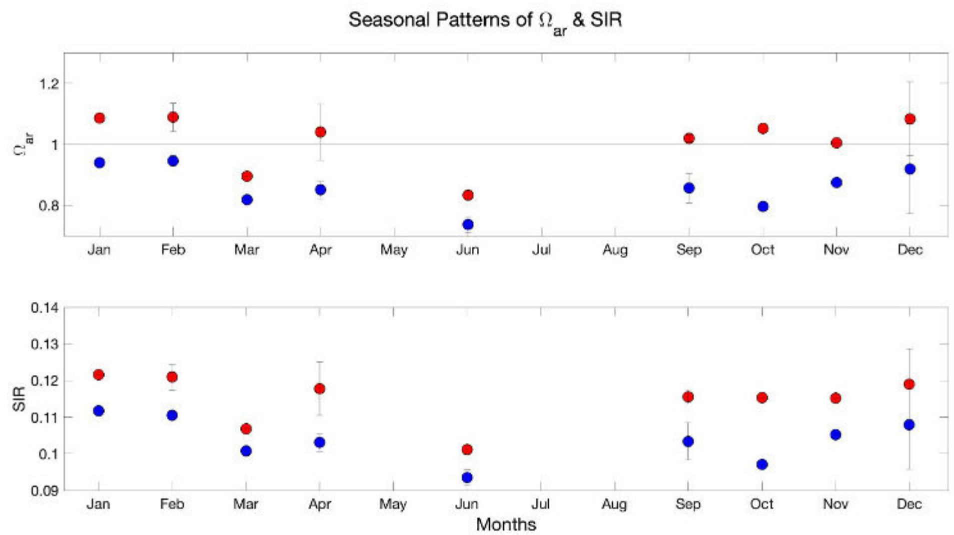

Figure 6. Seasonal variation of Ω_{arag} and SIR over the 4 different years. The top panel of Ω_{arag} shows the average values of each month in the upper 20 meters in red and between 100-200 meters in blue. There is a horizontal line at one indicating where the threshold is. The bottom panel of SIR also displays the average values of each month in the upper 20 meters in red and between 100-200 meters in blue.

Final Conclusions

In this preliminary study it was found that the algorithms performed generally well in both a qualitative analysis and a bias assessment by depth. Particularly CANYON-B performed well and was applied to the underwater glider data study OA conditions in the CCS (Figure 2a-2b). Furthermore, in order to assess the quality of the glider transect of interest the oxygen, salinity and temperature data was plotted with the high quality WCOA cruise data from 2016 and the positive overlap at depth is motivation that the following conclusions are trustworthy (Figure 3a-3b).

The current Ω_{arag} and SIR demonstrate that corrosive and undersaturated waters are washing up the continental shelf in an upwelling event (Figure 4-5). Therefore, benthic communities are being exposed to poor conditions for calcification and are simultaneously subjected to conditions that enhance dissolutions (Cai et al., 2020). While this is only an example of one transect, this finding is important because upwelling is expected to intensify and low Ω_{arag} and SIR values will shoal up the shelf impacting the commercial shellfish industry (Hauri et al., 2013;Bakun et al., 2015).

Lastly, there was not enough data to have a good understanding of a view of the seasonal cycle of SIR and Ω_{arag} (Figure 6). However, the plot does show that Ω_{arag} values at depth are below the threshold of one and the SIR values at depth are lower than values in the upper 20 meters. With more glider data observation it will be possible to have a better understanding of the seasonal changes of SIR and Ω_{arag}. The findings specified in this text will help contribute to the project of a USCS PhD student.

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