

**Determining CO<sub>2</sub> Balance influenced by  
Upwelling and Primary Production in the  
Equatorial Pacific Region at 180° using CO<sub>2</sub> and  
O<sub>2</sub> flux**

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## **Abstract**

The oceanic carbon cycle is one of the most important mechanisms in controlling the Earth's climate as oceans take up to 30% of the carbon emissions, acting as a major sink. The ocean's biological and solubility pumps are responsible for carbon storage through air-sea interactions. However, a big source of carbon to the atmosphere is the Equatorial Pacific due to it being a region of upwelling where old carbon-rich waters from the deep sea are transported to the surface. This paper highlights the finding of the research conducted upon the RV Thompson from 2<sup>nd</sup> to 8<sup>th</sup> March, 2023 in the Equatorial Pacific along the 5°N to 5°S transect during the tail end of a La Niña event. In order to quantify the air-sea flux and the proportion of carbon balance affected by upwelling and primary production in this region, a 1-D carbon budget model in steady state was applied to the CO<sub>2</sub> and O<sub>2</sub> distributions between 2°N and 2°S at the dateline (180°). Gas transfer velocity and solubility coefficients were used to quantify the outgassing of CO<sub>2</sub> and to understand the correlation strength of these factors. Using the model, 96% of the flux of CO<sub>2</sub> is affected by upwelling and less than 4% is affected by primary production. The average  $F_{\text{CO}_2} = 0.0120 \text{ mol m}^{-2} \text{ day}^{-1}$  from 2°N to 2°S due to the proximity to the equator but the highest flux out of the system was  $0.0227 \text{ mol m}^{-2} \text{ day}^{-1}$ , recorded at 3°N with gas transfer velocity of CO<sub>2</sub>  $\sim 27 \text{ cm/hr}$  at a wind speed of 11 m/s, after which the wind speeds became relatively constant proceeding 2°N. This indicated that even though biochemical factors play a dominant role in regulating air-sea flux, physical factors such as wind are quite important as well.

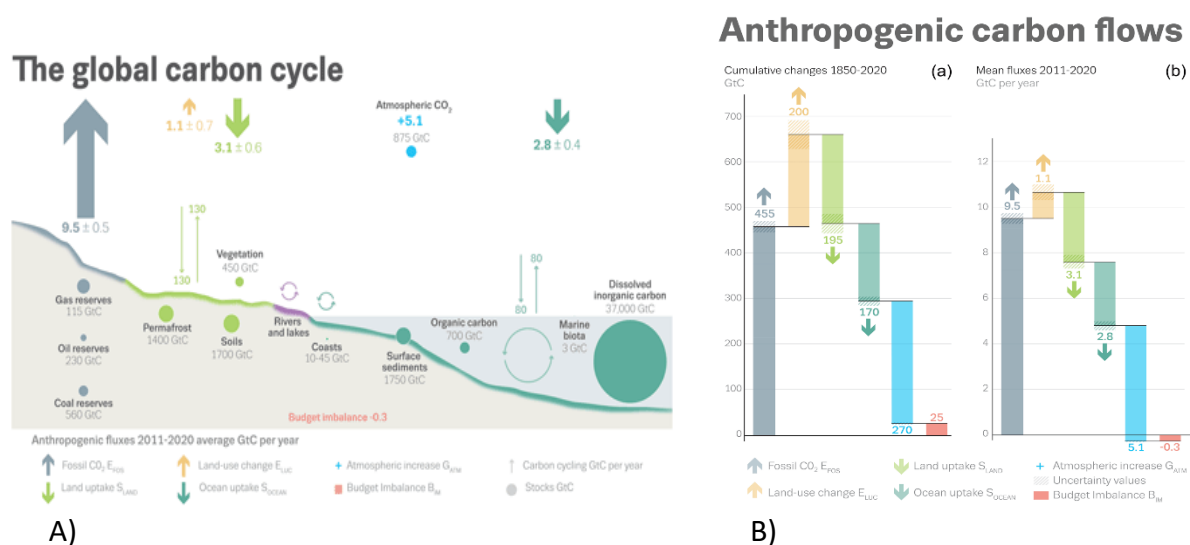
## **Plain Language Summary**

The oceans have been taking up carbon at a rapid pace over the last century and is predicted to keep doing so in order to compensate the anthropogenic emissions and regulate climate

change. The oceans are also a major source of oxygen as it contributes to almost half of the world's primary production and conversion of inorganic carbon to organic matter. However, one of the biggest sources of carbon is the equatorial Pacific, where carbon dioxide leaves the system rather than staying or being converted. To understand how the ocean interacts with the atmosphere, a simple carbon budget model is hypothesized to be calculated along the transect closest to the equator and with environmental conditions that are similar to each other (2°N to 2°S) at 180°. The model considers physical factors such as wind and salinity and also biochemical factors such as oxygen proxy for primary production and upwelling of carbon rich waters. This region was outgassing carbon, averaged out to a positive flux of  $0.01204 \text{ mol m}^{-2} \text{ day}^{-1}$  while the oxygen flux was averaged to be  $-0.000009 \text{ mol m}^{-2} \text{ day}^{-1}$ , implying that primary production was not able to overcome the amount of inorganic carbon being upwelled to the surface. Then using the estimated model, calculations showed that upwelling contributed to 96% of the flux while primary production contributed <4%. Furthermore, on an annual scale, the carbon flux =  $4.4 \text{ mol m}^{-2} \text{ yr}^{-1}$ , quite similar to previous studies conducted during muted El Niño events, with a flux out of the system. These factors together, can then help in understanding the magnitude of influence on carbon concentrations in the mixed layer and atmosphere, assuming steady state conditions, and possibly over large time scales as well if further research is conducted.

## Introduction

The global ocean is an integral component of the carbon cycle acting as a mediator between climate change and the planet's response to it. Over the course of the last 30 years, anthropogenic carbon emissions have been increasing and thus increasing the concentration of atmospheric carbon dioxide ( $\text{CO}_2$ ) (Hauck et al, 2020). Since the 1850s, the global ocean has taken up 26% of the atmospheric  $\text{CO}_2$  emissions



**Figure 1: Quantification of the A) carbon dioxide fluxes in the scope of the global carbon cycle from 2011-2020 and B) Mean carbon dioxide fluxes (GtC) from 2011-2020 using different sources (Friedlingstein et al, 2022)**

and recently in 2020 presumably contributed as one of the major carbon sinks by uptaking  $2.8 \pm 0.4 \text{ GtC yr}^{-1}$  in the past decade (Fig 1) (Friedlingstein et al. 2022). The  $\text{CO}_2$  gas interaction between the ocean and atmosphere is known as the air-sea flux and helps in equilibrating the  $\text{CO}_2$  (Gruber et al, 2009). It's one of the most predominant processes in determining the future of the carbon cycle and forecasting future  $\text{CO}_2$  concentrations (Takahashi et al, 2009).  $\text{CO}_2$  flux between the ocean and the atmosphere can help determine

climate-change models as well as estimation of shallow and deep-water exchange of CO<sub>2</sub> gas (Brady et al, 2019).

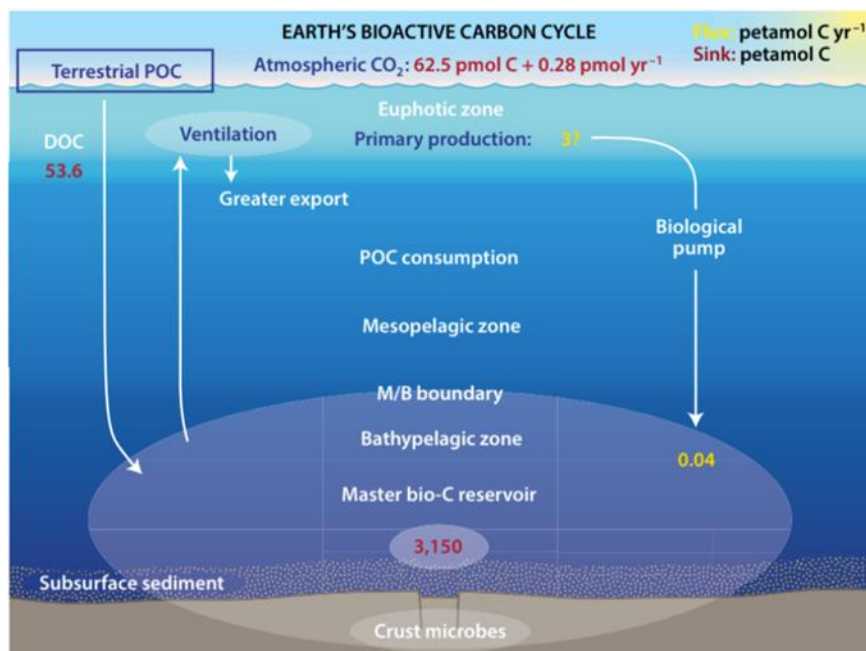


Figure 2: Diagram of the Carbon cycle and interaction of atmospheric CO<sub>2</sub> and biological pump (Honjo et al, 2014).

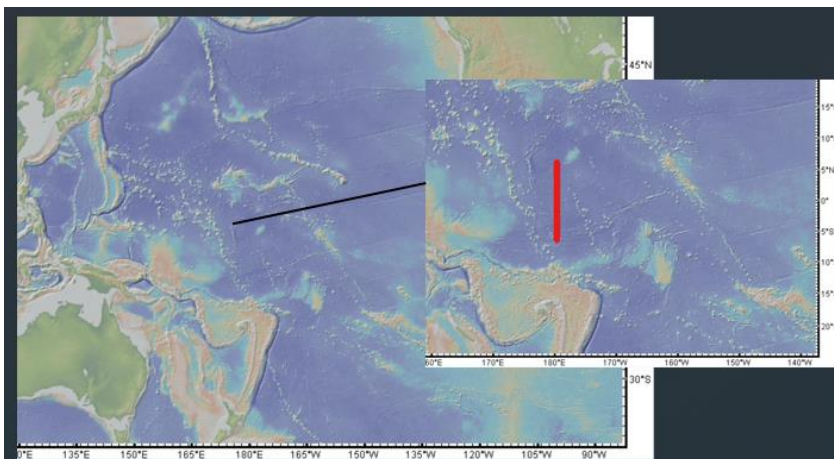
The thermodynamic equilibrium of dissolved CO<sub>2</sub> is maintained by the air-sea flux and can be quantified using the partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) (Gloege et al, 2022; Gruber et al. 2009; Sutton et al. 2017). To quantify the air-sea flux, which contributes to the global carbon cycle, measurement of partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) of both the atmosphere and ocean are utilized (Gloege et al, 2022 ; Gruber et al. 2009; Sutton et al. 2017). The difference in the pCO<sub>2</sub> of the atmosphere and the ocean

$$\Delta pCO_2 = [pCO_2]_{sw} - [pCO_2]_{atm} \quad (\text{Eq.1})$$

helps in quantifying the magnitude of  $\Delta pCO_2$  across the surface of the water as well as identify the sources and sinks of CO<sub>2</sub> (Takahashi et al, 2009). In order to determine the flux (F<sub>CO<sub>2</sub></sub>) itself, gas transfer velocity (k) (Wanninkhof, 2014) and solubility coefficient (K<sub>sol</sub>), which is dependent on sea surface temperature (SST) and sea surface salinity (SSS) (Weiss, 1974), also need to be taken into account as together they modulate the amount CO<sub>2</sub>

absorption into the ocean (Sutton et al, 2017;Tien et al, 2019). The value of  $k$  can be fit into an empirical function of wind stress, which is why it is essential to consider wind velocity in our calculations and data observations (Wanninkhof, 2014; Tien et al, 2019). It is important to note that surface ocean  $p\text{CO}_2$  can be perturbed by 3 main mechanisms, which then ultimately affect the overall flux: i) upwelling of cold  $\text{CO}_2$  rich waters from deep ocean leading to outgassing of  $\text{CO}_2$ , ii) the biological pump increasing its uptake of  $\text{CO}_2$  due to the influx of nutrients from the upwelled waters and ultimately converting dissolve inorganic carbon (DIC) to organic matter carried out by phytoplankton communities in the euphotic zone (Volk and Hoffert, 1985) (Fig.2) and the iii) solubility pump where during periods of relatively warmer surface waters the gas-exchange ability of  $\text{CO}_2$  is lowered and leads to a flux out of the ocean while cooler surface waters increases the solubility and positively intakes  $\text{CO}_2$  into the ocean (Friedrich et al, 2008 ; Heinze et al, 2015; Pittman et al, 2022; Volk and Hoffert,1985). Thus, air-sea flux provides an insight on the ocean's ability to act as a source or sink of  $\text{CO}_2$  and estimate the global carbon cycle changes and impacts.

Additionally, certain anthropogenically accelerated problems such as ocean acidification and algal blooms can also be expressed using the  $\text{CO}_2$  flux (Heinze et al, 2015).



**Figure 3: The red line spanning from 5N to 5S at Greenwich Meridian and has 15 data collection stations on that transect.**

In contrast, rather than a sink, the Equatorial Pacific is one of the biggest open ocean sources of CO<sub>2</sub> releasing ~0.5GtC of CO<sub>2</sub> yearly (Pittman et al, 2022; Takashi et al,2009; Wong et al, 2022) (<https://www.pmel.noaa.gov/co2/elNiño.html>). This region of the Equatorial Pacific (Fig. 3) is a region of wind-driven upwelling, which brings up cool rich DIC waters up to the surface thus increasing the pCO<sub>2</sub> in the surface ocean (Wong et al, 2022). Upwelling of nutrients in the equatorial Pacific drive the biological pump through high rates of primary production and uptake of CO<sub>2</sub> in dissolved inorganic form while also producing oxygen (O<sub>2</sub>) (Pittman et al, 2022; Volk and Hoffert, 1985). The O<sub>2</sub> flux then can be used as a proxy for primary productivity in this region, especially since most of the biological activity along with both CO<sub>2</sub> and O<sub>2</sub> fluxes, tend to occur in the mixed layer depth (MLD) (Emerson and Yang, 2022). However, there is still variability in the CO<sub>2</sub> concentrations interannually due to the El Niño-Southern Oscillation (ENSO) (Wong et al, 2022). ENSO is hypothesized to be the largest temporal variability in CO<sub>2</sub> flux as it can affect the thermocline depth and trade wind speed and how long the cold period lasts (Pittman et al, 2022)(<https://www.pmel.noaa.gov/co2/elNiño.html>). Generally, CO<sub>2</sub> outgassing is muted during El Niño and extremely elevated during La Niña events, the cold phase. This phase has stronger

and richer [DIC] waters being upwelled as well as stronger trade winds, driving a more positive CO<sub>2</sub> flux out of the ocean (Ayar et al, 2022; Pittman et al, 2022; Tian et al, 2019; Wong et al, 2022). Currently, the ENSO cycle in the Equatorial Pacific (Fig. 3) is nearing the end of the La Niña.

Although it is difficult to estimate the CO<sub>2</sub> flux due to various temporal, physical and biochemical factors all working together to influence the flux, this paper aims to provide a quantification of the  $\Delta p\text{CO}_2$  and primary productivity in order to understand a simple 1D carbon budget model in the Equatorial Pacific at 180°.

### **Hypothesis**

The equatorial Pacific at the International Dateline (180°) is a region of upwelling where CO<sub>2</sub> flux outgasses to the atmosphere as  $p\text{CO}_{2\text{SW}} > p\text{CO}_{2\text{Atm}}$ . Due to the equatorial Pacific being such a strong source of CO<sub>2</sub>, it's important to consider that surfacing waters are older have had mostly respiration occurring due to lack of sunlight, so nutrients such as dissolved O<sub>2</sub> concentrations may be significantly lowered.

However, this flux out of the ocean isn't the only sink for CO<sub>2</sub> as primary productivity also lowers the  $\Delta p\text{CO}_2$ , so then O<sub>2</sub> concentration and O<sub>2</sub> flux should be used to determine primary productivity in the mixed layer depth

Thus, if both CO<sub>2</sub> and O<sub>2</sub> budgets are measured using a simple model under constant pressure conditions at the surface, the total flux of CO<sub>2</sub> out of the water can be calculated as well as CO<sub>2</sub> flux out of the water only affected by primary production. I hypothesize then that I can quantify the proportion of the  $F_{\text{CO}_2}$  caused by upwelling and primary productivity and  $F_{\text{CO}_2}$  only caused by upwelling.

## Methods

### *1. Shipboard Measurements*

At each latitude, spanning from 5°N to 5°S (Table 1), Sea-Bird SBE 911 plus a conductivity, temperature and depth (CTD) instrument attached to a 24-positions rosette with 10L Niskin bottles was deployed and surface seawater temperature, surface sea water salinity and dissolved oxygen (using a SBE43 DO sensor) were collected at specific depths. Wind speeds (in knots) from 2<sup>nd</sup> to 8<sup>th</sup> March, 2023 were obtained using a sonic wind sensor mounted on the RV Thompson which collected wind speeds every 10 seconds. An underway  $\Delta p\text{CO}_2$  system was attached to the research vessel and measurements at each latitude were acquired using this system.

### *2. Underway $p\text{CO}_2$ System for $\Delta p\text{CO}_2$*

The instrument was operated by NOAA PMEL Ocean Carbon program. The system directed the flow of seawater through the equilibrator chamber where seawater  $\text{CO}_2$  equilibrated with the headspace gas in the chamber and then the  $\text{CO}_2$  in the headspace gas was measured via a non-dispersive infrared analyzer, where the  $\text{CO}_2$  mole fraction was obtained and then returned back to the equilibrator. The compound was calibrated using 4  $\text{CO}_2$  standard. Atmospheric gas was also pumped into the system to measure the  $\text{CO}_2$  mole fraction. These mole fractions were reported dry as the  $\text{CO}_2$  measurements were corrected with respect to the water vapor dilution and pressure effect internally by the analyzer itself (Pierrot et al, 2009).

### *3. Calibration of Oxygen*

Oxygen samples were titrated using a standard method (Codispoti, 1988) and calibrated. Calibration also aided in removal of poor and inconsistent data. Samples for analysis of dissolved O<sub>2</sub> concentrations were collected from 1000-150m with ~200m intervals and 5-100m with 30m intervals between the depths. At the equator, the samples were taken from 5-4000m with 1000m, 200m and 25m intervals.

The dissolved O<sub>2</sub> was titrated using a Metrohm Dosimat 665 Titrator and used to calibrate the oxygen concentrations and oxygen percent saturations. 3 sample standards were made and 1 blank correction factor as well.

### 3.1 Titration of Samples

i) A clean stir bar was added to the sample and then 1ml H<sub>2</sub>SO<sub>4</sub> was added and the solution was mixed well.

ii) The sample bottle was positioned on the stirrer with the buret tip submerged under the sample and the solution was titrated by dispensing thiosulfate into the sample. When the sample turned light yellow in color, 1ml of starch was added and the sample was titrated to the endpoint, when the solution turned sparkling clear.

iii) After the endpoint was recorded, the buret tip was rinsed with DI water to remove all residue.

### 3.2 Calibrating O<sub>2</sub> concentrations

In order to create a strong calibration, the titrated O<sub>2</sub> values were converted to μmol/kg and compared to the original O<sub>2</sub> sensor values. The O<sub>2</sub> concentrations obtained from the SBE43 sensor were then plotted against the titrated values and a calibration curve with a  $y=mx+b$

equation was found. ~18% of the values were anomalies and considered bad or random data and omitted from the calibration curve.

#### 4. CO<sub>2</sub> Flux calculation

CO<sub>2</sub> flux was quantified using the formula

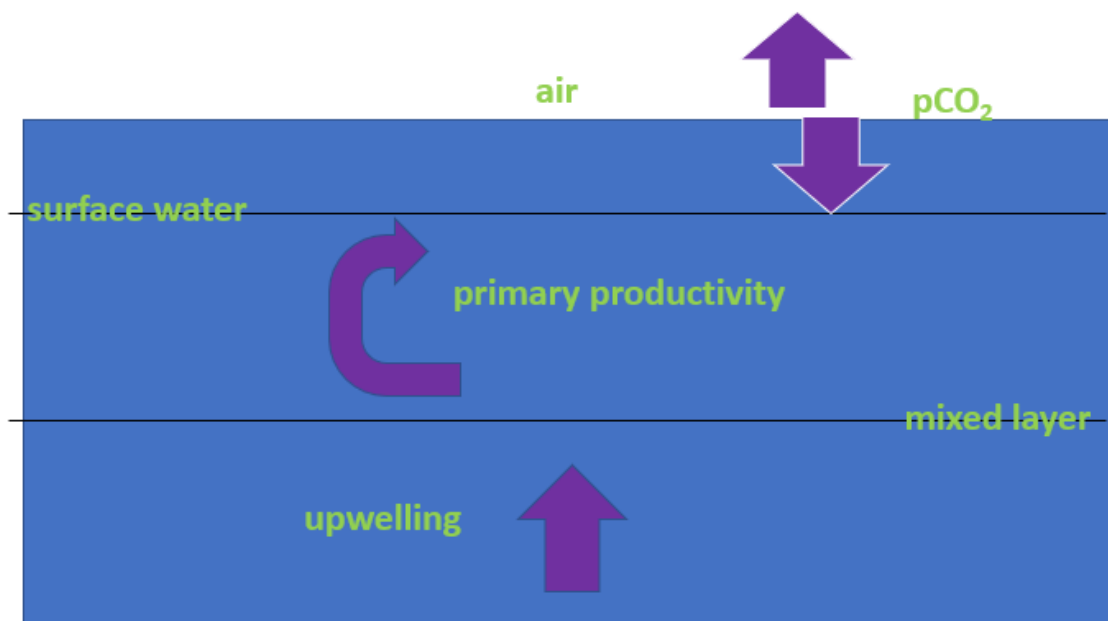
$$F_{CO_2} = k \times K_{sol} \times \Delta p_{CO_2} \quad (\text{Eq.2})$$

Gas transfer velocity, k was calculated using the relationship

$$k = 0.251 * (V_{10})^2 * \left(\frac{Sc}{660}\right)^{-0.5} \quad (\text{Eq.3})$$

where V is the wind speed and Sc is the Schmidt number of CO<sub>2</sub> or O<sub>2</sub> in seawater as a function of temperature (Wanninkhof, 2014). The Sc number was taken into account for the temperature variability and k was calculated according to those corresponding temperature of seawater for both the gases (Wanninkhof,1992). K<sub>sol</sub> for CO<sub>2</sub> was calculated using the empirical relationship between temperature, salinity and solubility estimated by Weiss (1974). However, as [O<sub>2</sub>]<sub>atm</sub> is considered constant, K<sub>sol</sub> for O<sub>2</sub> was estimated with respect to the concentration of O<sub>2</sub> in equilibrium with the atmosphere.

## 5. Carbon Budget Model Estimation



**Figure 4: Rough schematic of 1-D Carbon Budget Model and contribution of each factor towards the Carbon Dioxide Balance in the Equatorial Pacific region.**

A 1-D carbon budget model (Fig. 4) was estimated using a mixed layer model and the CO<sub>2</sub>:O<sub>2</sub> Redfield ratio. The model was quantified using

$$\frac{dC}{dt} = F + J + u\Delta C \quad (\text{Eq. 4})$$

where  $F$  is the gas dependent flux (Eq.2),  $J$  is the primary productivity factor,  $u\Delta C$  (inferred as  $U$  also) is the upwelling flux is the upwelling factor and  $\Delta C$  is the difference in concentrations from the deep and mixed layer (Emerson, 1987). For CO<sub>2</sub>, a consistent value of deep-water concentrations was used averaged over the whole research transect, and the mixed layer depth concentration values were obtained from another researcher aboard the RV Thompson (DIC concentrations) (T.Dominguez, personal communication, 2023) while for O<sub>2</sub>, the calibration curve equation was used to report the measured concentrations both in the mixed layer and below.

For simplification of the model, steady state was assumed ( $\frac{dC}{dt} = 0$ ), vertical advection and horizontal velocity along the mixed layer bottom boundary were assumed to be 0. To understand the proportion of the  $u$  and  $J$  and their contribution to the carbon budget, Eq.4 was modified in order to have 2 different simultaneous equations in the form of

$$u = \frac{-(F+J)}{C_d - C_{ml}} \quad (\text{Eq. 5}).$$

$J$  is the biological consumption factor for  $\text{CO}_2$  and the biological production factor for  $\text{O}_2$  due to primary production (Emerson, 1987). Thus, an assumption based on Redfield ratios were used to correlate the biological factor, where  $J_{\text{O}_2} = -\frac{-106}{138} J_{\text{CO}_2}$ .

To understand how strong upwelling or primary productivity contributes in the fluctuation of the carbon budget at the equator, the values of  $F$  and  $\Delta C$  were averaged from  $2^\circ\text{N}$  to  $2^\circ\text{S}$ .

## Results

In order to calculate the magnitude of the gas fluxes, the initial approach was to determine the average daily gas exchange coefficient. The wind speed ( $U$ ) m/s was then averaged out (using Coordinated Universal Time standards) to give the wind speed of each day.  $Sc$  value for  $\text{CO}_2 = 668$  and  $Sc$  value for  $\text{O}_2 = 568$  were used for  $k$  calculation (Wanninkhof, 1992 ; Wanninkhof, 2014). 2<sup>nd</sup> March was also included in the calculation to give an insight on the rate of change in wind speed and  $k$  values (Table 1). The wind speed significantly reduces going from 4<sup>th</sup> to 5<sup>th</sup> March and so do the  $k$  values of  $\text{CO}_2$  and  $\text{O}_2$ . The research vessel was approaching the Equatorial stations and transitioning into the Southern hemisphere, proceeding from 5<sup>th</sup> March and  $k$  is then observed to become relatively constant and have a lowered gradient change (Table 1).

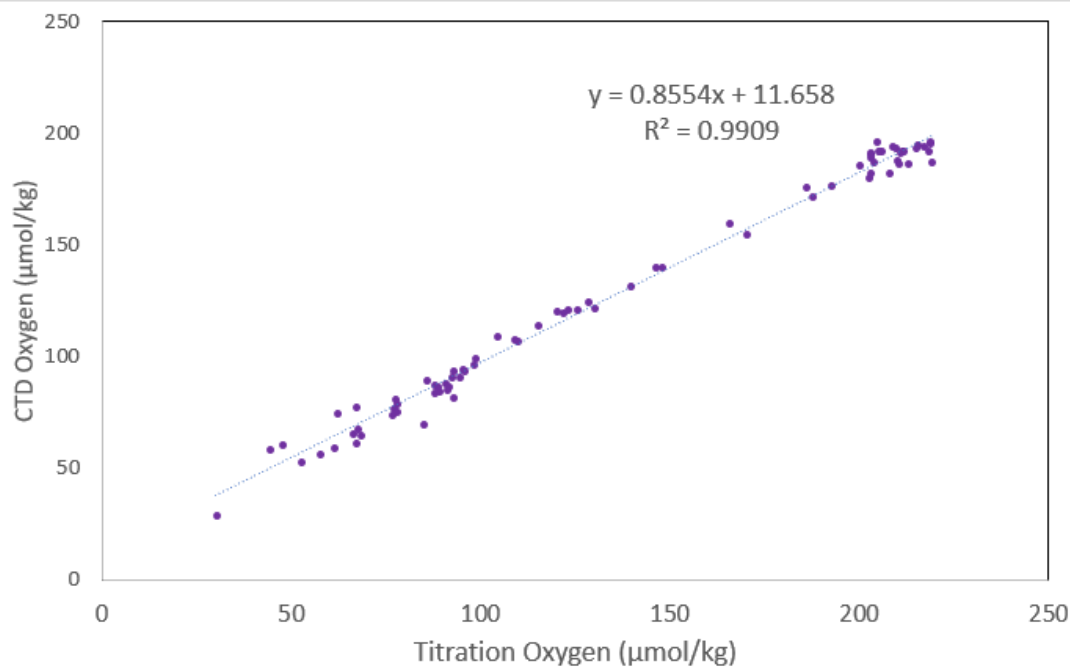
**Table 1: Daily Average wind speed (V) measured in m/s from March 2nd to 8<sup>th</sup>, 2023 and the corresponding Gas Transfer Velocities (k) measured in cm/hr for CO<sub>2</sub> and O<sub>2</sub> calculated at 180° based on the Sc temperature correlation, using UTC standard time. Positive latitudes correspond to the Northern Hemisphere and negative correspond to the Southern Hemisphere.**

Date	Latitude	V (m/s)	kCO <sub>2</sub> (cm/hr)	kO <sub>2</sub> (cm/hr)
2-Mar-23	6°	11.474	32.849	35.623
3-Mar-23	5°	9.410	22.091	23.957
4-Mar-23	4°	10.437	27.176	29.472
	3°			
5-Mar-23	2°	6.275	9.823	10.653
	1.5°			
	1°			
	0.5°			
	0°			
6-Mar-23	0°	6.225	9.667	10.484
	-0.5°			
	-1°			
	-1.5°			
	-2°			
7-Mar-23	-2°	6.563	10.747	11.654
	-3°			
	-4°			
	-5°			

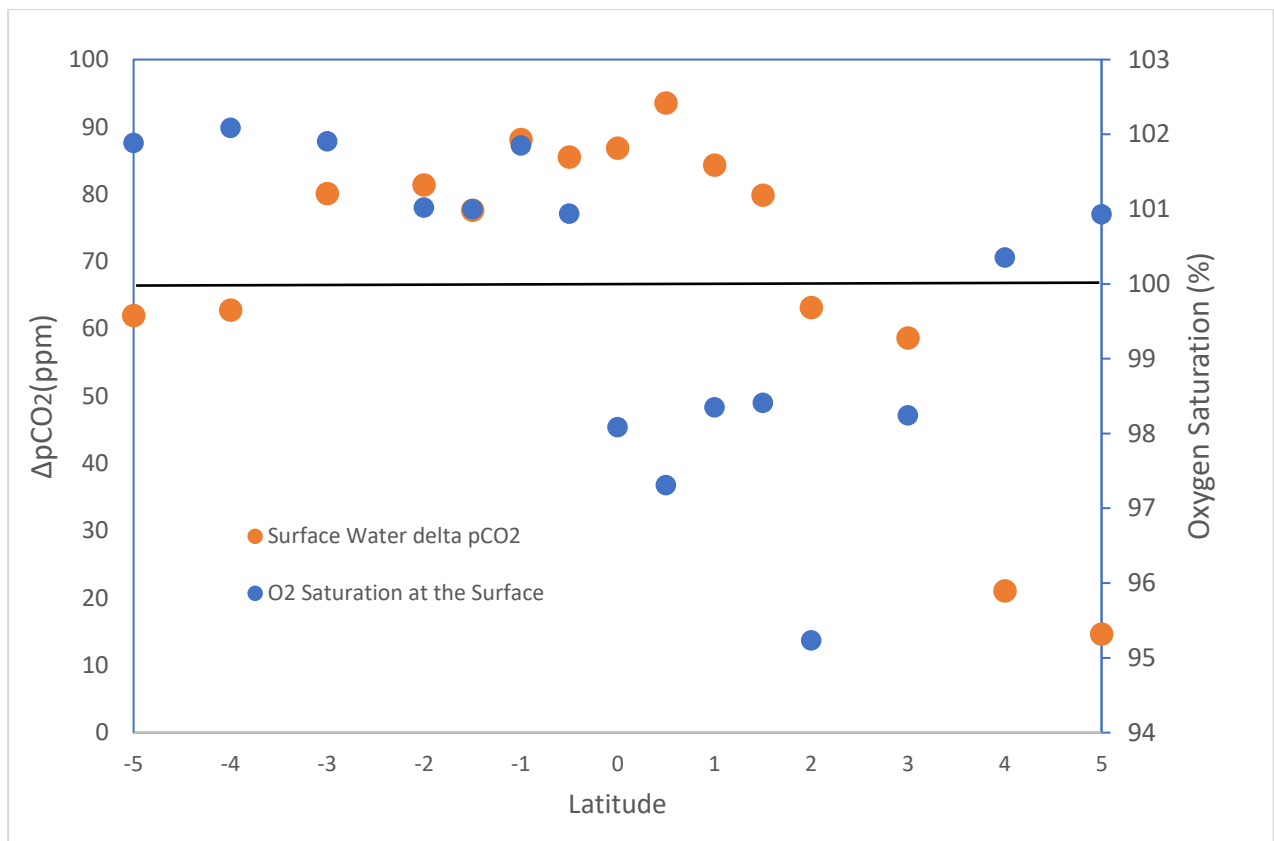
8-Mar-23	-5°	5.833	8.488	9.204
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The change in  $k_{CO_2}$  from 4<sup>th</sup> to 5<sup>th</sup> March is 17.35 cm/hr, which can be considered a steep gradient (Table 1).  $k_{CO_2} = 27.176$  cm/hr and  $k_{O_2} = 29.472$  cm/hr were the highest values recorded at  $V = 10.437$  m/s on 4<sup>th</sup> March, 2023 corresponding to 3°N and 4°N (Table 1). The lowest  $V = 6.225$  m/s and  $k_{CO_2} = 9.667$  cm/hr and  $k_{O_2} = 10.484$  recorded on 6<sup>th</sup> March, corresponding to stations at 0° to 2°S (Table 1).

**Figure 5: Calibration curve of the O<sub>2</sub> concentration (μmol/kg) collected using dissolved O<sub>2</sub> sensor 2 from March 3-8, 2023 along 5N to 5S at 180°**



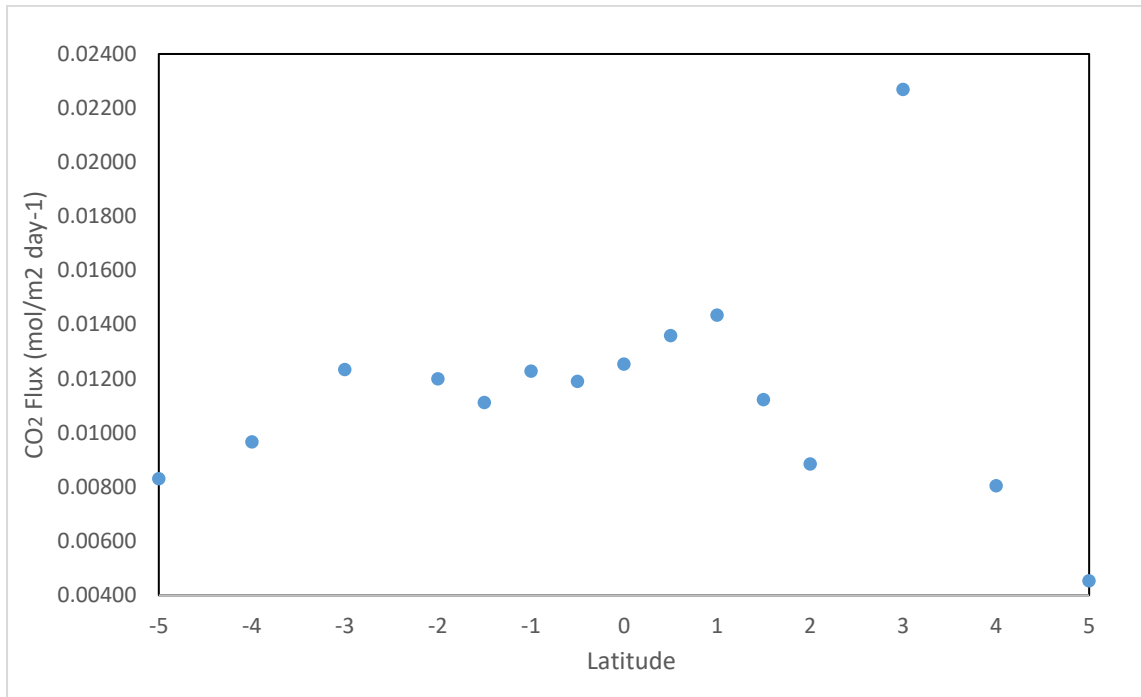
Dissolved O<sub>2</sub> values obtained from the SBE43 sensor were plotted against the titrated O<sub>2</sub> values to obtain a calibration curve (Fig 5). The equation of the line was used to convert the reported SBE43 dissolved O<sub>2</sub> concentrations and O<sub>2</sub> saturations to calibrated values.



**Figure 6: Surface Water CO<sub>2</sub> ΔpCO<sub>2</sub> in ppm (Orange) and O<sub>2</sub> saturation Percentage (Blue) from 5N to 5S at 180° from 3<sup>rd</sup>-8<sup>th</sup> March, 2023. Horizontal line drawn at 100% O<sub>2</sub> saturation.**

The average atmospheric pCO<sub>2</sub> during the survey was equal to 418.68ppm. ΔpCO<sub>2</sub> was plotted alongside the O<sub>2</sub> percentage saturation at the surface along the equatorial Pacific (Fig 6), where lowered oxygen saturation values are corresponding to a higher ΔpCO<sub>2</sub> closer to the equator(2°N - 2°S). The horizontal line differentiates the understaturated and saturated parts of equatorial Pacific, where anything below 100% O<sub>2</sub> saturation is undersaturated. The largest O<sub>2</sub> saturation gradient is at equator while the largest meridional gradient in ΔpCO<sub>2</sub> is at 3°N. The lowest ΔpCO<sub>2</sub> = 14.68ppm, corresponds to a high Sat<sub>O<sub>2</sub></sub> = 100.92 at 5°N. Closer to the equator (1°N - 1°S), ΔpCO<sub>2</sub> is the highest with relatively lowered Sat<sub>O<sub>2</sub></sub>, except at 1°S where O<sub>2</sub> saturation = 101.85% and ΔpCO<sub>2</sub> = 88.14ppm. The highest ΔpCO<sub>2</sub> = 93.55ppm at 0.5°N corresponding to a 97.31% of O<sub>2</sub> saturation. Even though, the lowest O<sub>2</sub> saturation =

95.23% was at 2°N with  $\Delta p\text{CO}_2 = 63.18$  ppm. As the transects moves from Northern equatorial Pacific to Southern Pacific, there's an increase in both  $\Delta p\text{CO}_2$  and  $\text{SatO}_2$  at the surface (Fig 6).



**Figure 7: Flux of CO<sub>2</sub> (mol m<sup>-2</sup> day<sup>-1</sup>) of surface seawater from 5°N to 5°S at 180° from 3<sup>rd</sup>-8<sup>th</sup> March, 2023.**

At 5°N,  $F_{\text{CO}_2} = 0.00454$  mol m<sup>-2</sup> day<sup>-1</sup> was recorded as the minimum calculated flux of CO<sub>2</sub> while at 3°N,  $F_{\text{CO}_2} = 0.0227$  mol m<sup>-2</sup> day<sup>-1</sup> was recorded as the highest flux of CO<sub>2</sub> (Fig 7). The daily flux in the Northern hemisphere further away from the equator is observed to be relatively lower than in the Southern hemisphere

Since the wind speed decreases dramatically from 3°N to 2°N (Table 1) and to create a simple C budget, the results for  $F_{\text{CO}_2}$  will be focused from 2°N - 2°S. The flux increases closer to the equator, with a peak at 1°N,  $F = 0.0144$  mol m<sup>-2</sup> d<sup>-1</sup> and then starts to gradually reduce transitioning from Northern transect into the Southern transect, except at 1°S, there's a slight peak with  $F = 0.0123$  mol m<sup>-2</sup> d<sup>-1</sup> (Fig 7).

**Table 2:  $\Delta$ DIC and  $\Delta$ O<sub>2</sub> measured in  $\mu$ mol/kg and their respective daily fluxes measured in mol m<sup>-2</sup> day<sup>-1</sup> from 2°N to 2°S between 5<sup>th</sup>-6<sup>th</sup> March, 2023 and the averaged values. Positive latitudes correspond to the Northern Hemisphere and negative correspond to the Southern Hemisphere.**

<b>Latitude</b>	<b><math>\Delta</math>DIC (<math>\mu</math>mol/kg)</b>	<b><math>\Delta</math>O<sub>2</sub> (<math>\mu</math>mol/kg)</b>	<b>F<sub>CO2</sub> (mol/m<sup>2</sup> day<sup>-1</sup>)</b>	<b>F<sub>O2</sub> (mol/m<sup>2</sup> day<sup>-1</sup>)</b>
2°	2118.440	-96.686	0.0088	-0.000051
1.5°	2074.400	-77.569	0.0112	-0.000012
1°	2062.631	-99.295	0.0144	-0.000021
0.5°	2032.191	-77.553	0.0136	-0.000022
0°	2050.232	-74.479	0.0125	-0.000015
-0.5°	2059.534	-101.438	0.0123	0.000010
-1°	2052.608	-73.430	0.0111	0.000013
-1.5°	2075.133	-105.291	0.0120	0.000011
-2°	2070.397	-84.811	0.0123	0.000008
<b>Average</b>	2066.174	-57.940	0.0120	-0.000009

The flux of CO<sub>2</sub> from 2°N to 2°S was then averaged = 0.0120 mol m<sup>-2</sup> day<sup>-1</sup> (Table 2). Average F<sub>O2</sub> = -0.000009 mol m<sup>-2</sup> day<sup>-1</sup> (Table 2). F<sub>O2</sub> from 2°N-0° is observed to be negative, which is a flux into the system while F<sub>O2</sub> starting from 0.5°S is calculated to be positive, a flux out of the system. Note that [CO<sub>2</sub>]<sub>deep</sub> = 2285  $\mu$ mol/kg and  $\Delta$ DIC were calculated based on this equilibrated [CO<sub>2</sub>]<sub>deep</sub> value.  $\Delta$ DIC and  $\Delta$ O<sub>2</sub> were multiplied by density (kg/m<sup>3</sup>) where the

mixed layer began, to convert into units of volume and then ultimately multiplied by  $k$  and  $K_{sol}$  to obtain the gas fluxes in  $\text{mol m}^{-2} \text{day}^{-1}$ .

Solving the system of equations for  $u$  and  $J$  using a variation of Eq.4 (Emerson, 1987) to account for the direction of the flux.

i)  $\text{CO}_2$

$$0 = -F[\text{CO}_2] + u(\Delta\text{CO}_2) - J[\text{CO}_2]$$

ii)  $\text{O}_2$

$$0 = -F[\text{O}_2] + u(\Delta\text{O}_2) - \frac{106}{138}J[\text{CO}_2]$$

$$0.00206617u - J = 0.01204$$

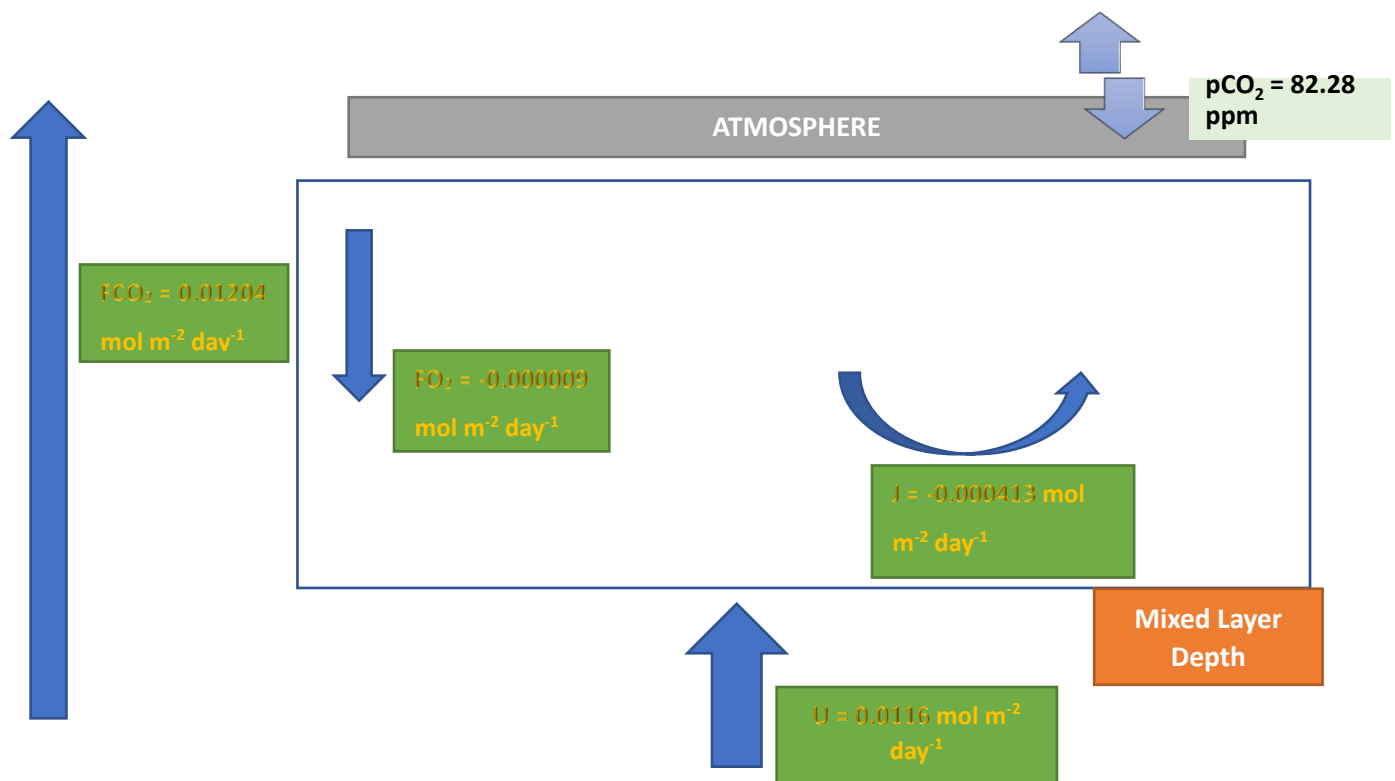
$$0.00005794u + 0.768J = 0.000009$$

$$u = 5.627$$

$$J = -0.000413 \text{ mol m}^{-2} \text{day}^{-1}$$

$$U = 0.0116 \text{ mol m}^{-2} \text{day}^{-1}$$

The overall upwelling term,  $U$  is equal to  $0.011 \text{ mol m}^{-2} \text{day}^{-1}$ , that is  $\sim 96.3\%$  of the  $\text{CO}_2$  flux while primary productivity,  $J$  contributes  $\sim 3.3\%$  towards the flux (Fig.8). The average  $\Delta p\text{CO}_2$  in this region was equal to  $82.3 \text{ ppm}$ .



**Figure 8: Schematic of 1-D Carbon Budget Model, interaction between atmosphere and the ocean,  $O_2$  and  $CO_2$  fluxes, and contribution of primary productivity ( $J$ ) and upwelling ( $U$ ) towards the Carbon Dioxide Balance in the Equatorial Pacific from  $2^\circ N$  to  $2^\circ S$ . All variables are in units of  $mol\ m^{-2}\ day^{-1}$  except  $pCO_2$  (ppm).**

To understand if the ENSO cycle (end of the La Niña) could potentially affect the  $CO_2$  and  $O_2$  fluxes, they were converted into an annual flux, where  $F_{CO_2} = 4.395\ mol\ m^{-2}\ yr^{-1}$  and

$F_{O_2} = -0.003285\ mol\ m^{-2}\ yr^{-1}$ , respectively in the Equatorial Pacific.

## Discussion

The ocean is one of the biggest sinks of  $CO_2$  and plays an integral role in maintaining the  $CO_2$  intereaction between the atmosphere and ocean, sequestering more than producing (Friedlingstein et al, 2022 ; Hauck et al, 2020). However, the equatorial Pacific is a unique region where  $CO_2$  leaves the system, or rather acts as a source for  $CO_2$  and outgasses into

the atmosphere (Pitmann et al, 2022). The CO<sub>2</sub> concentration is affected by many variables such as SST, wind speed, ENSO phases, upwelling and the primary productivity, where primary productivity acts as a sink.

### 1.1 Physical drivers of F<sub>CO<sub>2</sub></sub>

The average daily wind velocities seem to be decreasing as it gets closer to the equator (Table 1). Even though the winds are decreasing, the CO<sub>2</sub> flux is positive (Fig 7) and out of the system. According to Eq.2, the flux is dependent on k, the gas transfer velocity so the extremely high value of F<sub>CO<sub>2</sub></sub> at 3°N can be correlated more to high wind speeds and high k value (Fig 7) than ΔpCO<sub>2</sub> value of 58.63 ppm. When looking at previous studies conducted by NOAA Pacific Marine Environmental Laboratory (PMEL) in the equatorial Pacific, the yearly flux during a non-El Niño is positive and out of the system and is within the range of 0-7 mol m<sup>-2</sup> yr<sup>-1</sup>. The F<sub>CO<sub>2</sub></sub> = 4.4 mol m<sup>-2</sup> yr<sup>-1</sup> calculated during this research falls within that range, implying that this relatively cooler region is contributing to new CO<sub>2</sub> production and a stronger flux out of the oceanic system but is not entirely dependent on a neutral or La Niña phase as wind speeds significantly reduced starting from 2°N, indicating that other factors may be playing a bigger role in determining the positive outgassing of CO<sub>2</sub>.

### 1.2 ΔpCO<sub>2</sub> and O<sub>2</sub> saturation

Dissolved O<sub>2</sub> values were calibrated in order to reduce errors and standardize the concentrations without too much variability. Due to the upwelled waters being rich in DIC concentrations, it can explain how O<sub>2</sub> is undersaturated in this equatorial region (Fig.6). MLD being source of CO<sub>2</sub> due to nutrient-rich waters being transported up the water column would lead to a higher rate of primary productivity and ultimately higher O<sub>2</sub> production (Sutton et al,2017) but that did not seem the case at this specific time period. Additionally,

$J \approx -0.0004 \text{ mol m}^{-2} \text{ day}^{-1}$  implies that rather than primary productivity being a sink for carbon, it essentially is negligible in the carbon budget since it is contributing <4% to the  $\text{CO}_2$  flux. The negative magnitude also implies that there may have been a higher rate of respiration, where oxygen was being consumed faster than being produced (Emerson and Yang, 2022 ; Honjo et al, 2014). This lowered saturation of  $\text{O}_2$  could also explain the negative  $F_{\text{O}_2}$  averaged over  $2^\circ\text{N}$  to  $2^\circ\text{S}$  (Table 2). In contrast, the  $\Delta\text{pCO}_2$  values are increasing moving from  $2^\circ\text{N}$ , peaking at  $0.5^\circ\text{N}$ , staying above the 100% saturation line (Fig 6) and then gradually reducing when leaving the main equatorial basin. Additionally,  $F_{\text{CO}_2}$  is also dependent on the positive  $\Delta\text{pCO}_2$  (Eq 1), which implies that the  $[\text{CO}_2]$  in seawater was much more than the atmosphere (Fig 5), thus providing evidence that the equatorial Pacific is a source of  $\text{CO}_2$  and that rate of primary production is not able to overcome the rate at which  $\text{CO}_2$  is being upwelled. Another thing to note is that from  $2^\circ\text{N}$  to  $0^\circ$ ,  $\text{O}_2$  sat is under 100%, which could explain the negative  $F_{\text{O}_2}$  in the Northern Hemisphere from  $2^\circ\text{N}$  to  $0^\circ$  (Fig 6, Table 2) as there is just not enough  $\text{O}_2$  being produced.

The relatively higher  $\Delta\text{pCO}_2$  values can also be used to understand the low  $\text{O}_2$  saturation percentage, where higher rates of respiration are occurring and primary production is still taking place but not dominating the biological pump's effect on carbon storage.

### 1.3 Upwelling and $F_{\text{CO}_2}$

Previous studies by Sutton and Pittman provide evidence that upwelled DIC can be distributed in various ways throughout the ocean system, either by outgassing, advecting horizontally or exported to the deep ocean. For this study conducted in the equatorial Pacific, upwelling of cold nutrient-rich waters leads to a  $\text{CO}_2$  flux leaving the system and ultimately being vertically moved out of the system. Upwelling accounts for more than 95%

of the flux exiting the system (Fig.8) and can be assumed to be the main driver of the CO<sub>2</sub> and increased saturation in surface and mixed layer waters. Averaged yearly

$F_{CO_2} = 4.4 \text{ mol m}^{-2} \text{ yr}^{-1}$  (2°N to 2°S) should be considered significant enough to perturb the C-cycle as the equatorial Pacific is huge and changes in CO<sub>2</sub> flux on an annual basis is mainly caused by rate of upwelling(<https://www.pmel.noaa.gov/co2/elNiño.html>). It should be acknowledged that there were time constraints during the course of the research and various steady-state assumptions, especially related to horizontal advection of water and were included in the calculations in order to create a 1-D C budget model.

The highest recorded flux of CO<sub>2</sub> was at 3°N (Fig 6) but when only considering the transect 2°N to 2°S, the highest flux out of the system was at 1°N, which is interesting as the highest  $\Delta pCO_2$  was at 0.5°N (Fig 5) and both the stations at these latitudes had the same k value (Table 1). The only difference was the  $\Delta CO_2$  values (Table 2).  $\Delta CO_2$  for 1N = 2062  $\mu\text{mol/kg}$  while 0.5°N = 2032  $\mu\text{mol/kg}$ . This implies that at 1°N, the surface waters were slightly more saturated with CO<sub>2</sub> than at 0.5°N.

Upwelling played a substantial role in determining the carbon budget model in the equatorial Pacific and even though primary production was not as significant in budgeting the carbon concentrations, my hypothesis was able to be proved and that was the quantification of  $\Delta pCO_2$  in order to calculate the outgassing of CO<sub>2</sub> and understand the significance of upwelling and primary productivity's contribution to the carbon budget balance in the equatorial Pacific. If it was also possible, I would have liked to utilize advection of air-sea flux to determine analytically how much could heat contribute to the carbon balance (Wong et al, 2022). This 1-D carbon model does not have different sources of

atmospheric carbon entering the ocean and is rather equilibrated to one value but if it did, it could extend the scope of the budget model even more.

If time and resources permitted, chlorophyll and nutrients such as iron or nitrogen could also have been analyzed to understand the anomalous nature of primary productivity and how this phenomenon was not able to act as a strong sink for  $\text{CO}_2$  or even a strong source for  $\text{O}_2$ . Additionally, using Emerson's mixed layer formula variables such as MLD height and the vertical transport across the bottom boundary layer could potentially provide even more accurate values for upwelling and primary production fluxes which ultimately influence the C balance of the ocean, specifically the equatorial Pacific.

## **Conclusion**

A carbon budget model is utilized to understand the effects of different factors, be it biological or physical on the carbon cycle and how proportionately they contribute to the C concentrations, either in the ocean or out of the ocean. The ocean is generally a sink of  $\text{CO}_2$ , uptaking it to carry out primary production and stabilize the C-cycle. However, a unique region such as the equatorial Pacific acts as source of  $\text{CO}_2$  instead due to the high rates of upwelling, which brings up nutrient rich waters from the deep ocean to the mixed and surface layers. This phenomenon then tends to increase the concentrations, which leads to a flux of  $\text{CO}_2$  out of the system, or outgassing. The equatorial Pacific is a source of  $\text{CO}_2$  and sink of  $\text{O}_2$ . Even though physical factors such as  $k$  and  $K_{\text{sol}}$ , which is dependent on salinity are considered, it is evident that upwelling seems to play the biggest role in influencing the rate of change in carbon concentration ~96% of the flux. Additionally, wind speed and  $k$  also dropped sharply 27 cm/hr at 3°N to 9.8 cm/hr at 2°N and then stayed relatively even ~9cm/hr closer to the equator. This implied that wind could not have perturbed the  $F_{\text{CO}_2}$

immensely and cause the surface waters to be extremely saturated. But rather, it was the upwelling flux, that affected the CO<sub>2</sub> outgassing event from the equatorial Pacific. It is important to acknowledge that during periods of high upwelling, where DIC rich waters are surfacing, the water is expected to be undersaturated in O<sub>2</sub> which led to F<sub>O<sub>2</sub></sub> = -0.000009 mol m<sup>-2</sup> day<sup>-1</sup>. However, it is surprising that even though the rate of nutrient and DIC influx into the mixed layer is high, the biological factor, J = -0.0004 mol m<sup>-2</sup> day<sup>-1</sup> has a negative flux, indicating that primary production may not be occurring at a rate fast enough to counter upwelled waters. But on an annual scale, the F<sub>CO<sub>2</sub></sub> = 4.395 mol m<sup>-2</sup> yr<sup>-1</sup> is well within the expected range during a non-El Niño event. Difference in ENSO phases and how a warm phase vs a cold phase can really affect CO<sub>2</sub> saturation state and upwelling rates. Using the model which considers ΔpCO<sub>2</sub>, the daily CO<sub>2</sub> flux and primary production through an O<sub>2</sub> proxy, can be insightful towards future models of open oceans and their contribution to the carbon budget and aid in quantifying natural vs anthropogenic sources of CO<sub>2</sub> and their proportion of contribution towards climate change, increase in global temperatures and even ocean acidification due to increased uptake of inorganic carbon.

In a broader sense, the equatorial Pacific is an open ocean source of carbon but as anthropogenic emissions for CO<sub>2</sub> continuously rise, it is possible that due to the inability to overturn inorganic carbon to organic matter fast enough, many other parts of the ocean may become a source as well rather than a sink. Therefore, to understand how the atmospheric concentration of CO<sub>2</sub> is changing with respect to the ocean in upwelling regions, further studies could be conducted for prolonged periods of time to truly determine if the equatorial Pacific will remain a strong source of outgassing CO<sub>2</sub> system, even when compared to other areas of upwelling or could it possibly also act as a sink, depending on the strength of the biological and solubility pumps.

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