

# **The Complex Role of Storms in Modulating Air-Sea CO<sub>2</sub> Fluxes in the sub-Antarctic Southern Ocean.**

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## **Key Points:**

- Hourly glider observations show that the impact of storms on both  $k_w$  and  $\Delta pCO_2$  simultaneously modulates the magnitude of  $FCO_2$  variability.
- Winter-spring storms weaken  $\Delta pCO_2$  through enhanced entrainment and mixing, counteracting the expected increase in  $FCO_2$  due to  $k_w$  alone.
- By not accounting for the storm feedback in both  $k_w$  and  $\Delta pCO_2$ , the magnitude of the  $FCO_2$  was found to be overestimated (by 6.6 - 26.5%).

## **Abstract**

The intra-seasonal CO<sub>2</sub> flux ( $FCO_2$ ) variability across the Southern Ocean is poorly understood due to sparse observations at the required temporal and spatial scales. Twinned Waveglider-Seaglider experiments were used to investigate how storms influence  $FCO_2$  through both the gas transfer velocity ( $k_w$ ) and the air-sea gradient in partial pressure of CO<sub>2</sub> ( $\Delta pCO_2$ ) in the sub-Antarctic zone. Winter-spring storms caused  $\Delta pCO_2$  to weaken (by 15-55  $\mu atm$ ) due to mixing/entrainment and weaker stratification. This response in  $\Delta pCO_2$  was in phase with  $k_w$  resulting in a counteractive weakening in  $FCO_2$  (by 6.6 - 26.5% per storm), despite the wind-driven increase in  $k_w$ . Stronger stratification during summer explained the weaker sensitivity of  $\Delta pCO_2$  to storms, instead its thermal drivers dominated the  $\Delta pCO_2$  variability. These results highlight the importance of observing synoptic-scale variability in  $\Delta pCO_2$ , the absence of which may propagate

significant biases to the mean annual  $\text{FCO}_2$  estimates from large-scale observing programmes and reconstructions.

## Plain Language Summary

The sub-Antarctic zone of the Southern Ocean is a region that mostly experiences carbon dioxide ( $\text{CO}_2$ ) uptake because of its low temperature and strong winds. The wind can influence the  $\text{CO}_2$  uptake through two pathways: the speed of  $\text{CO}_2$  transfer between the air-sea interface ( $k_w$ ) and the difference in  $\text{CO}_2$  concentration in the surface ocean and overlying atmosphere ( $\Delta p\text{CO}_2$ ). Using autonomous robots that can measure hourly air and water conditions simultaneously, we show that not resolving  $\Delta p\text{CO}_2$  during a storm event can lead to overestimating the  $\text{CO}_2$  uptake. This is particularly important during winter and spring when the ocean's surface layers are less stratified. The warmer temperatures during summer meant a more stratified surface layer resulting in a weaker and delayed impact of storms on the  $\Delta p\text{CO}_2$ . This study shows that the various annual  $\text{CO}_2$  uptake estimation methods used by the research community should not neglect  $\Delta p\text{CO}_2$  responses during storms.

## 1. Introduction

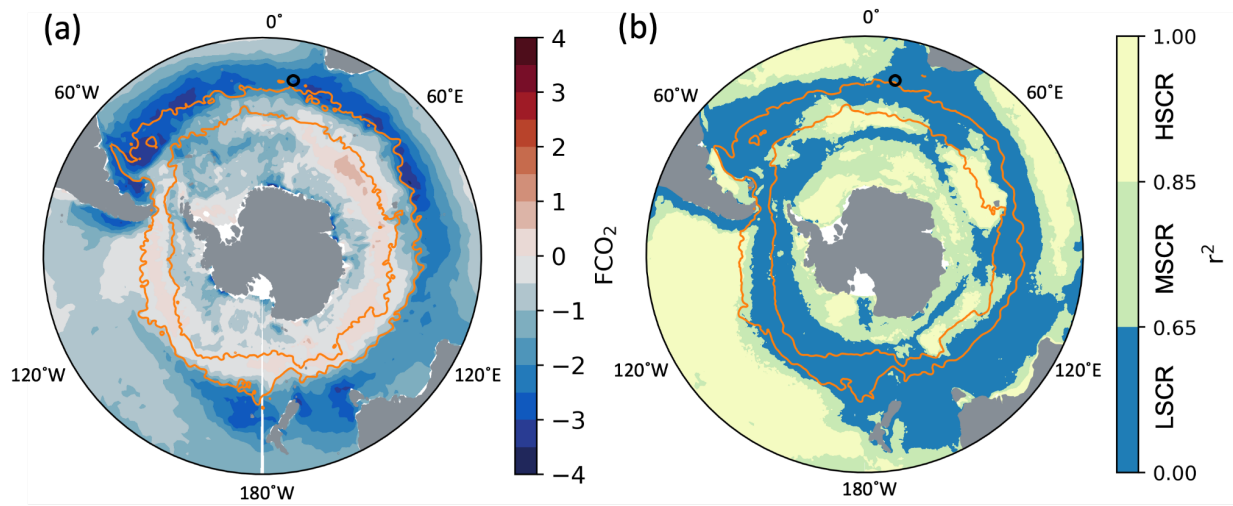
The sub-Antarctic zone (SAZ) of the Southern Ocean (SO) is a critical region in the global carbon cycle due to its ability to uptake ( $\sim 1 \text{ Pg C yr}^{-1}$ ) large amounts of anthropogenic  $\text{CO}_2$  (Figure 1a; DeVries et al., 2017; Gruber et al., 2019). Extra-tropical cyclones (hereafter referred to as storms) are prevalent synoptic features in the SO that occur at a 4 to 8-day frequency (Yuan, 2004; Wei & Qin, 2016; Lodise et al. 2022). These frequent storm events induce short but strong wind stress over the surface ocean which triggers several high-frequency (hourly to 10 days) responses at the air-sea and ocean-mixed layer interfaces, which have been shown to impact the air-sea  $\text{CO}_2$  flux ( $\text{FCO}_2$ ) significantly (Monteiro et al. 2015, Nicholson et al. 2022). However, despite the persistence of strong storms across the SO, few studies have investigated and quantified the role of storms on the  $\text{FCO}_2$  in the SAZ, particularly under different seasonal settings.

$\text{FCO}_2$  is governed by a bulk formulation which constitutes of the gas transfer velocity ( $k_w$ ) (Ho et al. 2006; Wanninkhof, 2014), the solubility constant ( $k_o$ ) (Weiss, 1974) and the gradient between the partial pressure of  $\text{CO}_2$  in the ocean ( $p\text{CO}_{2\text{sea}}$ ) and in the atmosphere ( $p\text{CO}_{2\text{air}}$ )

( $\Delta p\text{CO}_2 = p\text{CO}_{2\text{sea}} - p\text{CO}_{2\text{air}}$ ). The passage of a storm is likely to trigger responses to each of these bulk terms, which may occur in-phase (response time is the same) or out-of-phase (response time is different) with one another. During a storm, strong wind stress will result in stronger  $k_w$  (quadratic function of wind speed; Wanninkhof et al. 2014), increasing the magnitude of  $\text{FCO}_2$ . Importantly, the increase in wind stress may also generate upper ocean dissipation (through shear production and buoyancy loss) which elicits physical transport within and across the mixed layer and its boundaries. This is via vertical (entrainment) and lateral (advection) exchanges of water masses into and out of the mixed layer, increasing or decreasing  $p\text{CO}_{2\text{sea}}$  and  $\Delta p\text{CO}_2$  (Ito et al. 2016; Nicholson et al. 2022). A ‘buoyancy-dominated’ phase typically follows this ‘momentum-dominated’ phase of the storm. The quiescence period post-storm results in a loss in momentum through the drop in wind stress and a gain in buoyancy due to restratification. This can decrease  $k_o$  and increase  $p\text{CO}_{2\text{sea}}$  as the solubility of  $\text{CO}_2$  decreases (Sarmiento & Gruber, 2006). Above all, it may allow for an increase in the net primary productivity resulting in a net decrease in  $p\text{CO}_{2\text{sea}}$  post-storm during summer (Swart et al. 2015; Nicholson et al. 2016, Carranza et al. 2018; Nicholson et al. 2019; Uchida et al. 2020).

Evidence of storm-driven responses to bulk flux terms has been documented in the subpolar SO, a region of annual mean  $\text{FCO}_2$  outgassing (Nicholson et al. 2022). There, strong storm-induced wind stress was linked to increases in  $\text{FCO}_2$  through the  $k_w$  parameter but also because of concurrent upper ocean mixed layer entrainment of carbon-rich waters, rapidly modifying (reversing and changing the magnitude) the  $\Delta p\text{CO}_2$ , to result in strong outgassing events (Nicholson et al., 2022). Whether storms drive similar responses to both  $k_w$  and  $\Delta p\text{CO}_2$ , as well as the phasing of the response of these bulk flux terms, and how it impacts the  $\text{FCO}_2$  in the SAZ is yet unclear. However, some insights have been provided by Monteiro et al. (2015) through a conceptual figure, which linked storms to intra-seasonal variations of  $\text{FCO}_2$ , hypothesizing that storms in the SAZ triggered  $p\text{CO}_{2\text{sea}}$  to increase through entrainment, decreasing the magnitude of  $\Delta p\text{CO}_2$ , causing the  $\text{FCO}_2$  ingassing to slightly weaken despite the strong wind stress induced by the storm.

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**Figure 1:** (a) The air-sea CO<sub>2</sub> flux (FCO<sub>2</sub>), averaged from monthly CSIR-ML6 data (Gregor et al. 2019) from August 2015 to February 2016, the study period. Negative FCO<sub>2</sub> (in shades of blue) indicates the ingassing of CO<sub>2</sub> and positive FCO<sub>2</sub> (in shades of red) represents the outgassing of CO<sub>2</sub>. (b) The spatial characteristics of the seasonal cycle reproducibility (SCR) (method adapted from Thomalla et al. 2011) of pCO<sub>2</sub><sub>sea</sub> obtained from 10 years (2000 to 2009) of NEMO-PISCES simulations, highlighting the low SCR ( $r^2 = 0$  to 0.65; LSCR) of pCO<sub>2</sub><sub>sea</sub> in the majority of the Sub-Antarctic Zone (SAZ). The black circle represents the location where the SOSCEX-III experiment was conducted and the orange contours represent the northern and southern extent of the SAZ from the sea surface height-based definition of the sub-Antarctic Front and the Polar Front (Sokolov & Rintoul, 2009).

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Due to the regularity of these storms, such intra-seasonal variability is thought to dominate the seasonality of pCO<sub>2</sub><sub>sea</sub>, a dominant driver of FCO<sub>2</sub> variability, across large regions of the SO (Figure 1b; Monteiro et al. 2015; Gregor et al. 2019; Djeutchouang et al. 2022, Nicholson et al. 2022). However, because of the lack of high-frequency (< 10 days) observations throughout the SO, the mechanisms behind the intra-seasonal variability of FCO<sub>2</sub>, that link the storm-driven variability in wind stress directly to the FCO<sub>2</sub> are still not well understood. There remains some debate on what scales of variability are key to accurately estimate the annual mean FCO<sub>2</sub>. It has been argued that observed high-frequency variability in  $k_w$  only (available using high-resolution reanalysis wind products) is sufficient to capture the intra-seasonal responses of FCO<sub>2</sub> and the corresponding synoptic variability of pCO<sub>2</sub><sub>sea</sub> is of secondary importance to the overall FCO<sub>2</sub> estimates (Bushinsky et al. 2019). Observational evidence from other studies has shown that the phasing of both  $k_w$  and pCO<sub>2</sub><sub>sea</sub> to a storm event is important (Monteiro et al. 2015; Nicholson et al. 2022). This suggests that a 10-day or more sampling period may not necessarily capture storm-linked responses on the annual FCO<sub>2</sub> estimates and a sampling resolution of less than 3 days may

be more appropriate to capture such responses in 27.5% of the SO (Djeutchouang et al. 2022) to reduce the annual FCO<sub>2</sub> mean uncertainty to less than 10% (Monteiro et al. 2015).

In this study, we investigate the intra-seasonal changes in FCO<sub>2</sub> associated with storms and hypothesize that the wind-driven constraints on the FCO<sub>2</sub> through rapid modifications of pCO<sub>2sea</sub> may be as decisive as the high-frequency responses in the  $k_w$  parameter. Using high-resolution hourly glider observations, we first provide an explanation of the mechanisms that drive the pCO<sub>2sea</sub> variability during storms in the SAZ and then proceed to show the importance of considering the temporal aliasing of the pCO<sub>2sea</sub> and  $k_w$  to the strong winds on the FCO<sub>2</sub>.

## 2. Materials and Methods

### 2.1 Data collection

This study utilized data collected during the third Southern Ocean Seasonal Cycle Experiment (SOSCEX-III) in the SAZ (Further description in text S1 and refer to Swart et al. 2012). This experiment involved the simultaneous deployment of two Liquid Robotics Wave Gliders (WG) (CSIR1 and CSIR2) and two buoyancy profiling Seagliders (SG542 and SG543), which sampled roughly at 8.5°E and 43°S to simulate a pseudo-mooring pattern (Figure S1a).

The WGs sampled from 14th August to 17th October 2015 (CSIR1) and from 9th December 2015 to 8th February 2016 (CSIR2), covering the late winter to the end of the summer period. A modified MAPCO<sub>2</sub> sensor made both atmospheric (xCO<sub>2air</sub>) and oceanic (xCO<sub>2sea</sub>) observations at hourly temporal resolution with a precision of less than 2 µatm (Sutton et al. 2014). An Airmar XW-200 Ultrasonic Weather station recorded meteorological parameters at 10-minute intervals (further details in Schmidt et al. 2017). The weather station on CSIR1 WG was however faulty, and hourly ERA5 reanalysis wind speed data was used instead (Text S2 elaborates on the choice of reanalysis product).

The Seagliders conducted a total of 1832 profiles over 196 days, measuring the conductivity, temperature, and pressure, amongst others (see Thomalla et al. (2017) for more details), of the first 1000m of the ocean in a V-shaped pattern at a dive cycle of approximately 5

hours. These two deployments resulted in a continuous sampling from 28 July to 8 December 2015 (SG543) and 8 December 2015 to 8 February 2016 (SG542).

## 2.2 Estimation of the bulk CO<sub>2</sub> flux

The exchange of CO<sub>2</sub> (FCO<sub>2</sub>) between the surface ocean and atmosphere can be estimated using a bulk flux formula.

$$FCO_2 = k_w k_o (pCO_{2sea} - pCO_{2air}) \quad (1)$$

where  $k_w$  (cmhr<sup>-1</sup>) is the wind-driven gas transfer velocity (Wanninkhof, 2014),  $k_o$  (molL<sup>-1</sup>atm<sup>-1</sup>) is the solubility of CO<sub>2</sub> in seawater (Weiss, 1974),  $pCO_{2sea}$  and  $pCO_{2air}$  represent the partial pressure of CO<sub>2</sub> in the ocean and the atmosphere respectively.  $pCO_{2sea} - pCO_{2air}$  is commonly represented as  $\Delta pCO_2$ . Text S2 and S3 describe the quality control and method of calculations of each parameter of the bulk formula.

## 2.3 Thermal and non-thermal decomposition of $pCO_{2sea}$

$pCO_{2sea}$  was decomposed into its thermal ( $pCO_{2-th}$ ;  $\mu atm$ ) and non-thermal ( $pCO_{2-nt}$ ;  $\mu atm$ ) components (Takahashi et al. 1993, 2002).  $pCO_{2-th}$  accounts for the thermodynamically dependent characteristics of CO<sub>2</sub> which are driven by the variability in sea surface temperature (SST) while  $pCO_{2-nt}$  accounts for the biophysical processes (vertical mixing and biological consumption) which change the concentration of Dissolved Inorganic Carbon (DIC) in seawater (Takahashi et al., 1993).

$$pCO_{2-th} = pCO_{2sea-mean} \times e^{(0.0423(SST-SST_{mean}))} \quad (2)$$

$$pCO_{2-nt} = pCO_{2sea} \times e^{(0.0423(SST_{mean}-SST))} \quad (3)$$

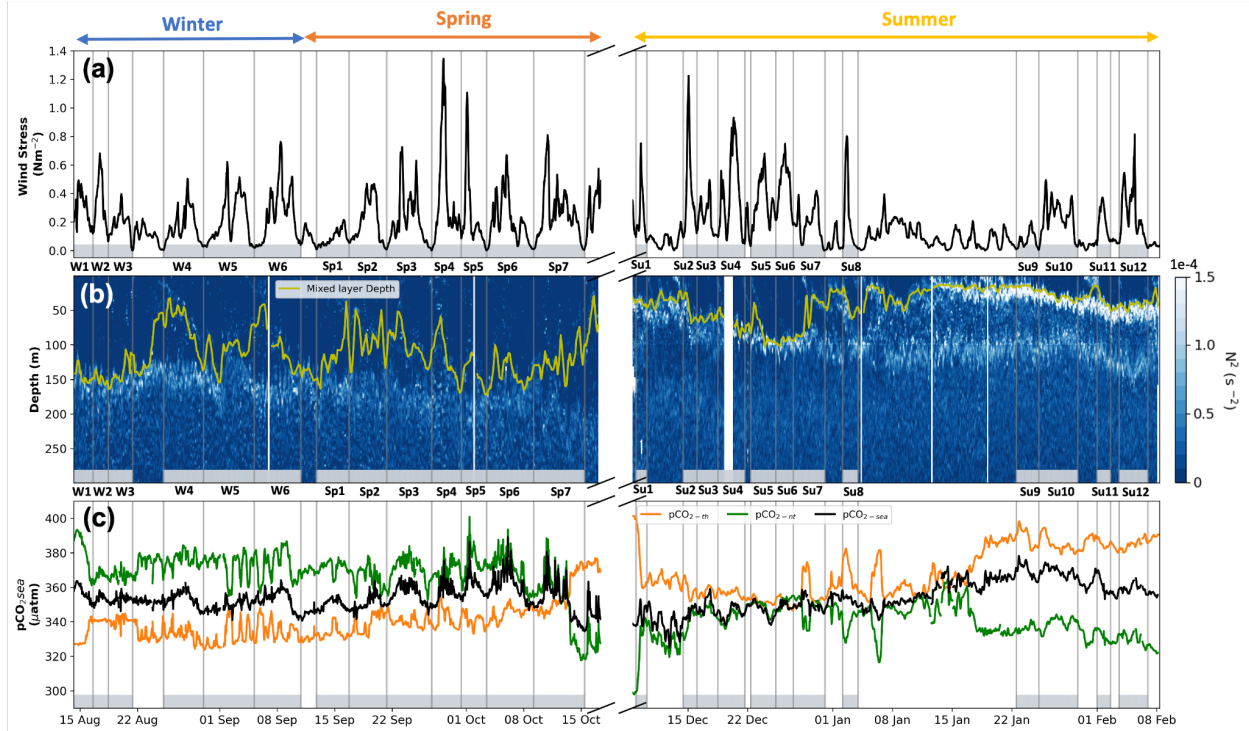
where  $pCO_{2\text{sea-mean}}$  and  $SST_{\text{mean}}$  are the mean of  $pCO_{2\text{sea}}$  and SST values throughout the entire study period respectively.

### 3. Results and Discussion

#### 3.1 Observed $pCO_{2\text{sea}}$ variability in response to storms.

Here we examine qualitatively how the synoptic-scale momentum-buoyancy dynamics influence the phasing of  $pCO_{2\text{sea}}$  responses to storms in the SAZ over a significant part of a seasonal cycle. To highlight the atmospheric forcing and upper ocean responses linked to storms, wind stress (a proxy for momentum fluxes), upper ocean stratification ( $N^2$ ) (a proxy for buoyancy fluxes), and the mixed layer depth (MLD) (momentum-buoyancy balance) were examined (Figures 2a and b). The  $pCO_{2\text{sea}}$  was also decomposed into its thermal ( $pCO_{2\text{-th}}$ ) and non-thermal component ( $pCO_{2\text{-nt}}$ ) to differentiate biophysical responses ( $pCO_{2\text{-nt}}$ ) from changes in SST ( $pCO_{2\text{-th}}$ ) (Figure 2c).

The study period was characterized by three seasonal regimes (winter, spring, and summer) that represented three different responses of  $pCO_{2\text{sea}}$  to storms (Figure 2c). During winter,  $pCO_{2\text{-th}}$  and  $pCO_{2\text{-nt}}$  showed considerable high-frequency response modes (between 1 to 6 hours), at time scales shorter than the wind stress variability (Figures 2a and c). Such high-frequency modes of variability ( $\pm 5\text{-}10 \mu\text{atm}$  in both  $pCO_{2\text{-th}}$  and  $pCO_{2\text{-nt}}$ ) can be indicative of the presence of both sub-mesoscale features ( $O$ ; 1-10 km) (Mahadevan et al. 2004; Lévy et al. 2012) and near-inertial motions (Alford et al. 2016) in the region. Sharp density gradients associated with sub-mesoscale features are short-lived (a few hours to days) and can induce strong vertical advection and mixing (Thomas et al. 2008), which can drive synoptic scale variations in the  $pCO_{2\text{-nt}}$  as seen in Figure 2. Similarly, near-inertial waves energised by storms trigger surface vertical mixing on timescale close to the inertial period (17.5 hours at  $43.5^\circ\text{S}$ ), also driving synoptic changes in the  $pCO_{2\text{-nt}}$  (e.g., during W5 and W6, Song et al. 2019, Nicholson et al. 2022).



**Figure 2:** (a) Time series of ERA5 Wind Stress ( $\text{Nm}^{-2}$ ) collocated to the gliders' location at  $8.5^{\circ}\text{E}$  and  $43^{\circ}\text{S}$ . (b) Seaglider observed upper ocean stratification, Brunt Väisälä frequency ( $\text{N}^2$ ;  $\text{s}^{-2}$ ), and mixed layer depth (m; in yellow). Methods for  $\text{N}^2$  and MLD calculation can be found in text S3 in the Supplementary Information (c) Wave Glider observed  $\text{pCO}_{2\text{sea}}$  ( $\mu\text{atm}$ ; in black) and its thermal ( $\text{pCO}_{2\text{-th}}$  ( $\mu\text{atm}$ ); in orange) and non-thermal ( $\text{pCO}_{2\text{-nt}}$  ( $\mu\text{atm}$ ); in green). The seasonal regimes were defined as a negative net heat flux for winter, an increasing net heat flux for spring, and a stable positive net heat flux for summer (du Plessis et al. 2019). The grey shading highlights the duration of each storm event with storms labelled underneath (Winter: W1-W6, Spring: Sp1-Sp7, and Summer: Su1-Su12), and the grey vertical lines separate each storm (storm identification method can be found in text S4 in the Supplementary Information).

These rapid changes of DIC within the MLD are usually accompanied by rapid temperature changes (Figure 2c). The transport of subsurface water to the surface lowers the temperature within the mixed layer which can decrease the  $\text{pCO}_{2\text{-th}}$  (by increasing the solubility of  $\text{CO}_2$ , Sarmiento & Gruber, 2006), hence offsetting the effect of the transported DIC on the overall  $\text{pCO}_{2\text{sea}}$  (Mahadevan et al. 2004, Resplandy et al. 2009). Indeed, for most of winter, these high-frequency modes of variability have little impact on the  $\text{pCO}_{2\text{sea}}$  variability (Figure 2c), likely due to the  $\text{pCO}_{2\text{-th}}$  and  $\text{pCO}_{2\text{-nt}}$  terms cancelling each other out (Figure 2c). Instead, the net changes in  $\text{pCO}_{2\text{sea}}$  appear in phase with the wind stress variability linked to storms (Figures 2a and c). During W1 to W6, the  $\text{pCO}_{2\text{sea}}$  showed a small increase and consequent decrease ( $\pm 5\text{-}15 \mu\text{atm}$ ) with the synoptic wind stress cycle. A possible explanation is that the increasing wind stress generated deep mixing,



deepening the MLD (up to  $\sim 50$  m  $\text{day}^{-1}$ ; Figure 2b) and possibly entraining DIC into the surface mixed layer (as observed in Ko et al. 2021 and Nicholson et al. 2022). As the wind stress decreases post-storm, the mixed layer re-stratifies and shoals the MLD (e.g., between W3 and W4, Figure 2b) until the next storm and the cycle repeats itself. During spring or summer, this quiescent period between storms would typically lead to phytoplankton blooms (Monteiro et al. 2015; Carranza et al. 2018), causing a drop in  $\text{pCO}_{2\text{sea}}$  but the nearly abiotic conditions ( $< 400$  mg C  $\text{m}^{-2} \text{d}^{-1}$ , Figure S3) of the SAZ in winter allowed us to eliminate Net Primary Productivity (NPP) as a driver of the  $\text{pCO}_{2\text{sea}}$  changes observed. In addition to entrainment, wind-driven lateral advection of  $\text{pCO}_{2\text{sea}}$  could also drive the synoptic-scale responses in  $\text{pCO}_{2\text{sea}}$  (Figure 2b; Takahashi et al. 2009; Monteiro et al. 2015; Nicholson et al. 2022).

During spring, the intra-seasonal modes of variability in  $\text{pCO}_{2\text{-nt}}$  ( $\pm 50$   $\mu\text{atm}$ ) were much larger than those in  $\text{pCO}_{2\text{-th}}$  ( $\pm 15$   $\mu\text{atm}$ , Figure 2c). These stronger variations in  $\text{pCO}_{2\text{-nt}}$  were in turn reflected in the  $\text{pCO}_{2\text{sea}}$  (up to  $\pm 55$   $\mu\text{atm}$ , comparable to the seasonal variation in  $\text{pCO}_{2\text{sea}}$ ) which also varied in phase with the storm wind stress cycle ( $r^2 = 0.45$ , Figure 2a). These stronger bursts in  $\text{pCO}_{2\text{sea}}$  could be linked to more intense entrainment events occurring because of stronger storms ( $> 0.75$   $\text{Nm}^{-2}$ ; Figure 2a), and weaker stratification ( $< 0.5 \times 10^{-4}$   $\text{s}^{-2}$ , Figure 2b) in spring compared to winter ( $0.75$   $\text{Nm}^{-2}$  and  $0.5 - 1.0 \times 10^{-4}$   $\text{s}^{-2}$ ). These conditions favour stronger vertical mixing, entraining DIC into the mixed layer (Song et al. 2019; Nicholson et al. 2022). In addition to stronger storm-induced vertical mixing on  $\text{pCO}_{2\text{-nt}}$ , the surface net heat flux gradually increased towards the end of spring (du Plessis et al. 2019) leading to the  $\text{pCO}_{2\text{-th}}$  to also slowly increase because of warmer SST reducing the solubility of  $\text{CO}_2$  (Mahadevan et al. 2004). The contribution of this gradual increase in  $\text{pCO}_{2\text{-th}}$  and the storm-induced variation on  $\text{pCO}_{2\text{-nt}}$  led to the observation of the strongest  $\text{pCO}_{2\text{sea}}$  response during Sp6 ( $\pm 55$   $\mu\text{atm}$ ) (Figure 2c).

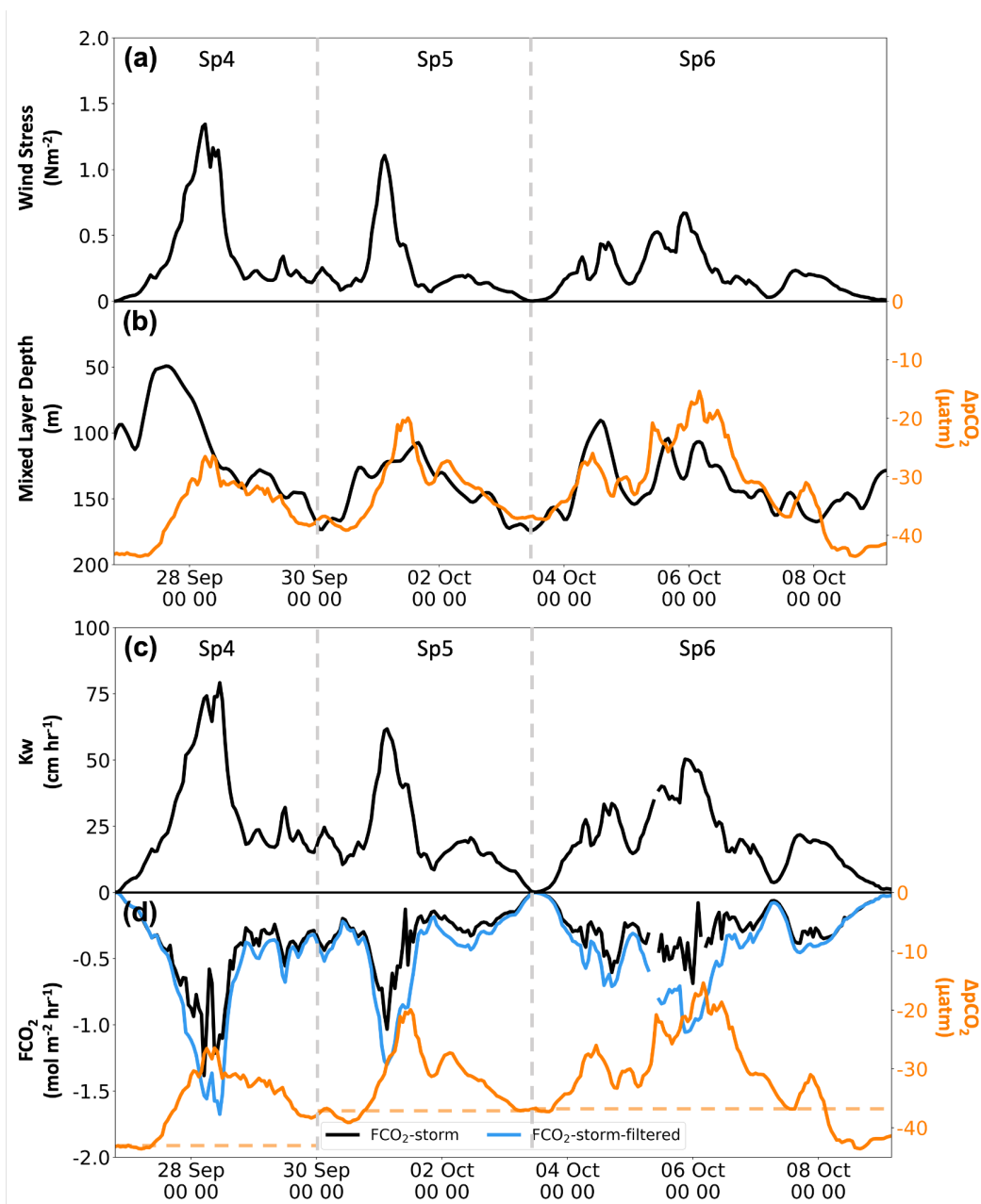
As the surface net heat flux increased further towards the end of spring (du Plessis et al. 2019), the MLD shoaled up to 50 m (Figure 2b).  $\text{pCO}_{2\text{-th}}$  was observed to exceed the  $\text{pCO}_{2\text{-nt}}$  on 13 October 2015 (Figure 2c), because of an increase in SST that caused the gradual increase in  $\text{pCO}_{2\text{-th}}$  and an increased consumption of DIC through NPP that led to the simultaneous gradual

decrease in  $p\text{CO}_{2-\text{nt}}$ . This reversal in the  $p\text{CO}_{2-\text{th}}$  and  $p\text{CO}_{2-\text{nt}}$  marked the transition from spring to summer regimes in the  $p\text{CO}_{2\text{sea}}$  variability 44 days before the seasonal mixed layer restratification took place (on 26 November 2015 in du Plessis et al. 2019). This highlights the seasonal transition in the primary drivers of  $p\text{CO}_{2\text{sea}}$  variability from a momentum-dominated winter to a combination of momentum and gradually increasing buoyancy-dominated spring ( $p\text{CO}_{2-\text{th}}$ ,  $r^2 = 0.02$ ) to finally a thermally and NPP-driven summer ( $p\text{CO}_{2-\text{th}}$ ,  $r^2 = 0.39$ ) (Figure 2c).

As expected, due to the increased solar radiation in summer, the pycnocline stratification strengthened ( $0.5 \times 10^{-4} - 1.0 \times 10^{-4} \text{ s}^{-2}$ ) and shoaled (50–100 m) during early summer and intensified ( $3.0 \times 10^{-4} - 4.4 \times 10^{-4} \text{ s}^{-2}$ ) and shoaled ( $\leq 50 \text{ m}$ ) further towards the end of summer (Figure 2b). As the late summer pycnocline layer shoaled and strengthened, the remnant of the winter pycnocline remained below it at approximately 100–150 m (du Plessis et al. 2019), disconnecting the deeper subsurface reservoir of higher DIC from the surface mixed layer (Sprintall et al. 1992; Swart et al. 2015). This could explain the reduced sensitivity of  $p\text{CO}_{2\text{sea}}$  to wind stress variations observed across summer (Figures 2a and c). The seasonal warming was also reflected in the slow rise in  $p\text{CO}_{2-\text{th}}$  (Mahadevan et al. 2004), with variations in  $p\text{CO}_{2-\text{nt}}$  observed during quiescent periods (e.g., between Su1 to Su2) because of consumption of DIC by high net primary productivity (Monteiro et al. 2015; Swart et al. 2015; Carranza et al. 2018; Nicholson et al. 2019; Figures 2c and S3).

### 3.2 The influence of the wind on both $k_w$ and $\Delta p\text{CO}_2$

Given that  $p\text{CO}_{2\text{sea}}$  responds so sensitively to storm-linked momentum fluxes during winter and spring, does it also influence the synoptic cycle of the  $\text{CO}_2$  flux ( $\text{FCO}_2$ ) relative to the wind stress? To examine this question, we focused on three consecutive storms (Sp4, Sp5, and Sp6), which occurred in spring (Figure 3).



**Figure 3:** Time series of (a) ERA5 Wind Stress ( $\text{Nm}^{-2}$ ), (b) Mixed Layer Depth (m; in black) and  $\Delta p\text{CO}_2$  ( $\mu\text{atm}$ ; in orange), (c)  $k_w$  ( $\text{cm hr}^{-1}$ ) and (d)  $\text{CO}_2$  flux,  $\text{FCO}_2$  ( $\text{mol m}^{-2} \text{hr}^{-1}$ ) as observed by the Wave Glider ( $\text{FCO}_{2\_storm}$ ; in black) and the storm-filtered  $\text{FCO}_2$  ( $\text{FCO}_{2\_storm\text{-filtered}}$  in blue) calculated from hourly  $k_w$  and pre-storm  $\Delta p\text{CO}_2$  (dashed orange line), for the duration of 3 spring storms events Sp4, Sp5 and Sp6 (27 September 2015 to 9 October 2015).

The variability in  $\Delta p\text{CO}_2$  is controlled by the air-sea gradient of  $p\text{CO}_{2\text{sea}}$  with negative values implying the ingassing of  $\text{CO}_2$ . Across the SO, the contribution made by  $p\text{CO}_{2\text{air}}$  variability to  $\Delta p\text{CO}_2$  is relatively low (1-4  $\mu\text{atm}$ , Tozawa et al. 2021), compared to the seasonal to intra-

seasonal variability in  $p\text{CO}_{2\text{sea}}$  (10-100  $\mu\text{atm}$ , Mongwe et al. 2016, Gregor et al. 2018). Furthermore, while storm linked atmospheric pressure can modulate the  $p\text{CO}_{2\text{air}}$  significantly, it also influences  $p\text{CO}_{2\text{sea}}$  (Text S2), resulting in the net impact of the atmospheric pressure on  $\Delta p\text{CO}_2$  to be insignificant. Therefore,  $p\text{CO}_{2\text{sea}}$ , and its drivers, have a decisive influence on  $\Delta p\text{CO}_2$  across the SO (Takahashi et al., 2009, Mongwe et al., 2016), and during the study period ( $r^2 = 1$ , Figures 2c and 3b). In response to an increase in wind stress,  $\Delta p\text{CO}_2$  weakened in magnitude (e.g. from -35 to -20  $\mu\text{atm}$  during Sp5) almost in phase with the wind stress with a short lag between each peak varying between 1 to 3 hours throughout all 3 storm events (Figure 3b; brown line). The response of the MLD was, in contrast, out of phase with the wind stress (Figure 3b) which was as expected and can be explained as the delayed response of the MLD due to inertial motion set by the passing storms (Cisewski et al. 2005) and the low responsiveness of the MLD to the wind stress when compared with the active mixing layer (Whitt et al. 2019; Nicholson et al. 2022).

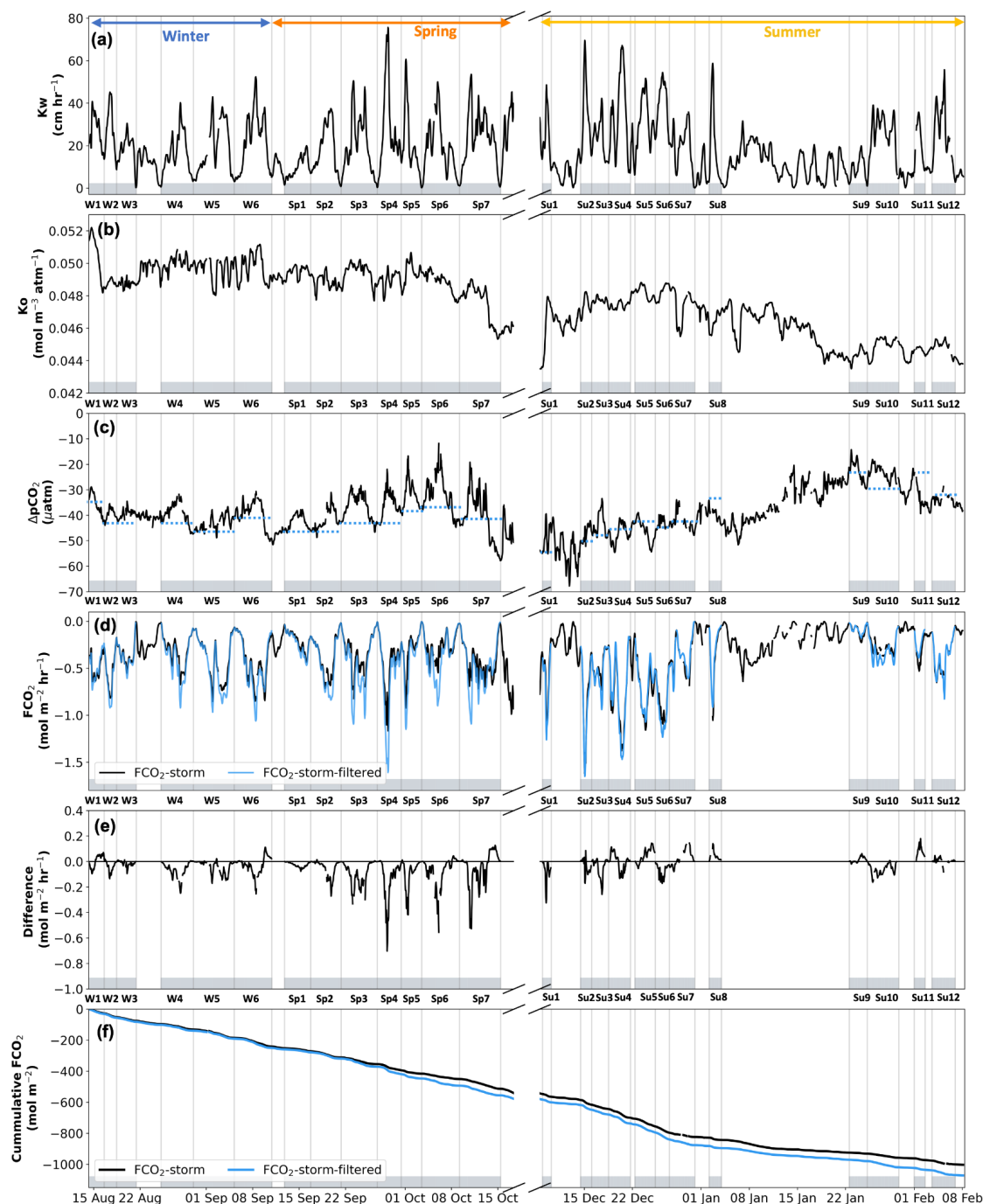
According to the bulk  $\text{FCO}_2$  formula, the influence of the wind on the  $\text{FCO}_2$  is accounted for through the nonlinear (quadratic) relationship between  $k_w$  and the wind speed (Wanninkhof et al. 2014). To examine our hypothesis about how, instead, the high-frequency variability of  $\Delta p\text{CO}_2$  and  $k_w$  are both necessary to capture the magnitude and phasing of the intra-seasonal mean  $\text{FCO}_2$ , we compared the observed  $\text{FCO}_2$  ( $\text{FCO}_{2\text{-storm}}$ ) and a calculated  $\text{FCO}_2$  which removes the mixing/entrainment response of  $p\text{CO}_{2\text{sea}}$  ( $\text{FCO}_{2\text{-storm-filtered}}$ ). The  $\text{FCO}_{2\text{-storm-filtered}}$  was re-calculated using hourly  $k_w$  but with  $\Delta p\text{CO}_2$  kept constant to its pre-storm value to filter out the storm-driven synoptic response of  $\Delta p\text{CO}_2$  (Figure 3d – blue line). For this study, using the pre-storm  $\Delta p\text{CO}_2$  was the best option (Text S4) as it mutes the influence of the previous and following storms on  $\Delta p\text{CO}_2$  during any storm to have a more accurate estimate of the  $\text{FCO}_2$  per storm event.

With each storm,  $k_w$  increases in phase with the wind stress (Figure 3c), which, in turn, drove the increase in magnitude of the  $\text{FCO}_2$  (Figure 3d, Wanninkhof et al. 2014). The phasing between  $\text{FCO}_{2\text{-storm}}$  and  $\text{FCO}_{2\text{-storm-filtered}}$  were similar, i.e., they both varied in phase with each storm because of  $k_w$  (Figure 3d). However, because  $\Delta p\text{CO}_2$  also weakened in response to the increasing wind stress, the magnitude of the  $\text{FCO}_{2\text{-storm}}$  was lower than the  $\text{FCO}_{2\text{-storm-filtered}}$ . This is also

consistent with the observations in Monteiro et al. (2015) where  $\text{FCO}_2$  was observed to weaken despite the increase in wind stress induced by storms. Bushinsky et al. (2019) suggested that the aliasing error from a 10-day sampling frequency of  $\text{pCO}_{2\text{sea}}$  (Monteiro et al. 2015) from biogeochemical profiling floats may not be the primary source of uncertainty in the annual  $\text{FCO}_2$  estimate in the SO because hourly wind speed data captures most of the intra-seasonal  $\text{FCO}_2$  variability through the  $k_w$  term. However, our study shows that, while the  $k_w$  term does capture most of the  $\text{FCO}_2$  variability, the temporal phasing of the  $\Delta\text{pCO}_2$  and the  $k_w$  throughout a storm event is both needed to not overestimate the intra-seasonal  $\text{FCO}_2$  (by up to  $0.7 \text{ molm}^{-2}\text{hr}^{-1}$  during the peak of storm Sp4) because the wind influences both the  $k_w$  and the  $\Delta\text{pCO}_2$  simultaneously (Figure 3d).

### 3.3 Seasonal-scale implications of storm-induced synoptic variability

The above experiment was replicated for the whole observed time series to further explore the implications of the complex storm-induced impacts on  $\Delta\text{pCO}_2$  on the integrated seasonal mean  $\text{FCO}_2$  (Figure 4). Since both  $k_w$  and the wind stress were calculated as a function of the wind speed, they were also strongly correlated ( $r^2 = 0.95$ ; Figures 2a and 4a). The overall contribution of  $k_o$  to the synoptic variability of  $\text{FCO}_2$  was shown to be very small throughout the study period ( $r^2 = 0.06$ ; Figure 4b). The synoptic scale variability in  $k_o$  (up to  $0.02 \text{ molm}^{-3}\text{atm}^{-1}$ ), was small compared to the magnitude of its seasonal variability (up to  $0.1 \text{ molm}^{-3}\text{atm}^{-1}$ ), both of which reflected changes in temperature and salinity instead (Figure 4b).



**Figure 4:** Time series of the (a) gas transfer coefficient,  $k_w$  ( $\text{cm hr}^{-1}$ ) calculated from ERA5 winds. Wave Glider observations of (b) solubility coefficient,  $k_o$  ( $\text{mol L}^{-1} \text{atm}^{-1}$ ), (c) gradient in the partial pressure of  $\text{CO}_2$  between the ocean and the atmosphere ( $\Delta p\text{CO}_2$  ( $\mu\text{atm}$ ) =  $p\text{CO}_{2\text{sea}}$  ( $\mu\text{atm}$ ) -  $p\text{CO}_{2\text{air}}$  ( $\mu\text{atm}$ )), (d)  $\text{CO}_2$  flux,  $\text{FCO}_2$  ( $\text{mol m}^{-2} \text{hr}^{-1}$ ) in black and the storm-filtered  $\text{FCO}_2$ , with the wind influence through  $k_w$  only, in blue, (e) difference between the observed  $\text{FCO}_2$  and the storm filtered  $\text{FCO}_2$  ( $\text{mol m}^{-2} \text{hr}^{-1}$ ), (f) Cumulative sum of the observed  $\text{FCO}_2$  (in black) and storm-filtered  $\text{FCO}_2$  (in blue). The grey shading represents the storm occurrences, and the grey lines separate each storm from one another.

Throughout the deployment,  $\Delta p\text{CO}_2$  was negative indicating a persistent ingassing flux of  $\text{CO}_2$ , characterized by a strong mode of synoptic-scale variability, at the sampling location (Figure 4c). The magnitude of the re-calculated  $\text{FCO}_{2\text{-storm-filtered}}$  (excluding the storm- $p\text{CO}_{2\text{sea}}$  feedback) was consistently stronger than the  $\text{FCO}_{2\text{-storm}}$  during winter-spring but much less so during summer events (Figure 4d). This is seen through the variability in the magnitude of the difference between the observed and re-calculated fluxes ( $\text{FCO}_{2\text{-storm}} - \text{FCO}_{2\text{-storm-filtered}}$ ) (Figures 4d and e). It shows that the difference in magnitude was weaker during winter (up to  $-0.3 \text{ molm}^{-2}\text{hr}^{-1}$ ) and strongest during spring (up to  $-0.7 \text{ molm}^{-2}\text{hr}^{-1}$ ) which also coincided with the pronounced synoptic variability in the  $p\text{CO}_{2\text{sea}}$  due to a combination of stronger storms ( $>0.75 \text{ Nm}^{-2}$ ), weaker stratification ( $<0.5 \times 10^{-4} \text{ s}^{-2}$ ) and the slow seasonal increase of the  $p\text{CO}_{2\text{-th}}$  component (Figure 2b and c). It also shows that the  $\text{FCO}_2$  averaged per storm event can be overestimated by a minimum of 6.6% (W3 and Sp1) to a maximum of 18.3% (W6) in winter and 26.5% (Sp4) in spring if the storm- $p\text{CO}_{2\text{sea}}$  feedback is omitted from the  $\text{FCO}_2$  (Figure 4e).

To examine the integrated impact of storms on the  $p\text{CO}_{2\text{sea}}$ , their cumulative influence on the  $\text{FCO}_2$  through most of a seasonal cycle was investigated. The cumulative sum of both the  $\text{FCO}_{2\text{-storm}}$  ( $-1003.06 \text{ molm}^{-2}$ ) and  $\text{FCO}_{2\text{-storm-filtered}}$  ( $-1069.47 \text{ molm}^{-2}$ ) across winter, spring, and late summer, also showed an overall overestimation bias of 6.41% (Figure 4f), suggesting that not accounting for the storm driven responses in  $p\text{CO}_{2\text{sea}}$  on the  $\text{FCO}_2$ , over a significant portion of a seasonal cycle, introduces a bias in the annual cumulative  $\text{FCO}_2$  uptake. At the study location, each storm had a lifespan of 1.5 to 7 days. Autonomous floats with a 10-day sampling frequency (Johnson et al. 2017) could thus have a limited probability ( $<10\%$ , Monteiro et al. 2015) of capturing the entire synoptic cycle of  $p\text{CO}_{2\text{sea}}$  (Figure 2c), resulting in the intra-seasonal  $\text{FCO}_2$  variability in the SAZ not being appropriately captured (Figure 4d, Monteiro et al. 2015, Djeutchouang et al. 2022). Our results provide an initial mechanistic analysis, which support the findings of Monteiro et al. (2015) (and thereafter Djeutchouang et al. 2022), showing why a 3-day or less sampling period is necessary to reduce the uncertainties in the annual mean  $\text{FCO}_2$  estimates in the SAZ.

This study was conducted in the SAZ, a region characterised by frequent storms and mesoscale features which disrupts the seasonal cycle of  $p\text{CO}_{2\text{sea}}$  leading to this region to be

dominated by intra-seasonal modes of  $p\text{CO}_{2\text{sea}}$  variability (Figure 1b; Monteiro et al. 2015, Gregor et al. 2019, Djeutchouang et al. 2022). From a Seasonal Cycle Reproducibility (SCR) metric (Figure 1b), formulated from a mesoscale resolving model for the SO, we thus propose that the findings of this study will project to the low SCR regions, which extends to 25 to 30% of the SO (Figure 1b), and emphasize the need for high frequency ( $< 3$  days)  $p\text{CO}_{2\text{sea}}$  observations in such regions.

#### 4. Synthesis

This study hypothesized that the influence of high-frequency wind variability induced by storms on  $p\text{CO}_{2\text{sea}}$  contributes significantly to mean estimates of  $\text{FCO}_2$  on seasonal to annual time scales. We showed that the wind simultaneously influences two terms of the  $\text{FCO}_2$  bulk equation:  $k_w$  and  $\Delta p\text{CO}_2$ , and that this influence was seasonally sensitive. Three main conclusions could be framed from this study.

First, the influence of the storm-driven wind on hourly  $p\text{CO}_{2\text{sea}}$  observations in the SAZ was strongly seasonal. Across winter and spring, the mechanistic response of  $p\text{CO}_{2\text{sea}}$  appeared mostly momentum-dominated, i.e., wind-induced entrainment and lateral advection during storm events drove most of its variability (Figure 2), with the influence of NPP being very small to undetectable (Figure S3). During summer,  $p\text{CO}_{2\text{sea}}$  variability seemed predominantly affected by NPP and changes in the SST, with  $p\text{CO}_{2\text{sea}}$  responses to the storm-driven wind variability being weakly sensitive (Figure 2). Future work and experiments will include observations of turbulent mixing to provide a more quantitative analysis of the associated mechanisms to discern the vertical entrainment of DIC from horizontal advection (e.g., Nicholson et al. 2022).

Second, based on these seasonally different mechanistic responses in  $p\text{CO}_{2\text{sea}}$ , storms have been shown to counterintuitively weaken the  $\text{FCO}_2$ , due to the weakening in the magnitude of  $\Delta p\text{CO}_2$ , despite the increase in  $k_w$ , throughout winter and spring (Figure 4). This highlights the



importance of sampling  $\Delta p\text{CO}_2$  at high frequencies to minimize a potential overestimation of the  $\text{FCO}_2$  uptake by up to 18.3% in winter and 26.5% in spring.

Finally, the integrated influence of these synoptic scale overestimations of the  $\text{FCO}_2$  over an entire seasonal cycle, showed that the cumulative sum of the strength of  $\text{FCO}_2$  uptake could be overestimated by 6.41% (Figure 4e) and this bias can be projected to 25 to 30% of the area of the SO (Figure 1).

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## Open Research

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