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# Anthropogenic CO<sub>2</sub>, air–sea CO<sub>2</sub> fluxes, and acidification in the Southern Ocean: results from a time-series analysis at station OISO-KERFIX (51° S–68° E)

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**Abstract.** The temporal variation of the carbonate system, air–sea CO<sub>2</sub> fluxes, and pH is analyzed in the southern Indian Ocean, south of the polar front, based on in situ data obtained from 1985 to 2021 at a fixed station (50°40′ S–68°25′ E) and results from a neural network model that reconstructs the fugacity of CO<sub>2</sub> ( $f\text{CO}_2$ ) and fluxes at monthly scale. Anthropogenic CO<sub>2</sub> ( $C_{\text{ant}}$ ) is estimated in the water column and is detected down to the bottom (1600 m) in 1985, resulting in an aragonite saturation horizon at 600 m that migrated up to 400 m in 2021 due to the accumulation of  $C_{\text{ant}}$ . At the subsurface, the trend of  $C_{\text{ant}}$  is estimated at  $+0.53 \pm 0.01 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$  with a detectable increase in the trend in recent years. At the surface during austral winter the oceanic  $f\text{CO}_2$  increased at a rate close to or slightly lower than in the atmosphere. To the contrary, in summer, we observed contrasting  $f\text{CO}_2$  and dissolved inorganic carbon ( $C_T$ ) trends depending on the decade and emphasizing the role of biological drivers on air–sea CO<sub>2</sub> fluxes and pH inter-annual variability. The regional air–sea CO<sub>2</sub> fluxes evolved from an annual source to the atmosphere of  $0.8 \text{ molC m}^{-2} \text{ yr}^{-1}$  in 1985 to a sink of  $-0.5 \text{ molC m}^{-2} \text{ yr}^{-1}$  in 2020. Over 1985–2020, the annual pH trend in surface waters of  $-0.0165 \pm 0.0040$  per decade was mainly controlled by the accumulation of anthropogenic CO<sub>2</sub>, but the summer pH trends were modulated by natural processes that reduced the acidification rate in the last decade. Using historical data from November 1962, we estimated the long-term trend for  $f\text{CO}_2$ ,  $C_T$ , and pH, confirming that the progressive acidification was driven by the atmospheric CO<sub>2</sub> increase. In 59 years

this led to a diminution of 11 % for both aragonite and calcite saturation state. As atmospheric CO<sub>2</sub> is expected to increase in the future, the pH and carbonate saturation state will decrease at a faster rate than observed in recent years. A projection of future  $C_T$  concentrations for a high emission scenario (SSP5-8.5) indicates that the surface pH in 2100 would decrease to 7.32 in winter. This is up to  $-0.86$  lower than pre-industrial pH and  $-0.71$  lower than pH observed in 2020. The aragonite undersaturation in surface waters would be reached as soon as 2050 (scenario SSP5-8.5) and 20 years later for a stabilization scenario (SSP2-4.5) with potential impacts on phytoplankton species and higher trophic levels in the rich ecosystems of the Kerguelen Islands area.

## 1 Introduction

The ocean plays an important role in mitigating climate change by taking up a large part of the excess of heat (Cheng et al., 2020a; Fox-Kemper et al., 2021) and of CO<sub>2</sub> released by human activities (Sabine et al., 2004; Gruber et al., 2019a; Canadell et al., 2021). Since 1750, the global ocean has captured  $185 \pm 35 \text{ PgC}$  (petagram of carbon) from a total of  $700 \pm 75 \text{ PgC}$  of anthropogenic carbon emissions from fossils fuels and land-use changes (Friedlingstein et al., 2022). The oceanic sink for anthropogenic CO<sub>2</sub> increased progressively from  $1.1 \pm 0.4 \text{ PgC yr}^{-1}$  in the 1960s to  $2.3 \pm 0.4 \text{ PgC yr}^{-1}$  in the 2000s. Over the decade 2012–2021, the partitioning

of the anthropogenic CO<sub>2</sub> uptake was roughly equal between the ocean ( $2.9 \pm 0.4 \text{ PgC yr}^{-1}$ ) and the land ( $3.1 \pm 0.6 \text{ PgC yr}^{-1}$ ) (Friedlingstein et al., 2022). This partitioning has been confirmed for the decade 2013–2022 (Friedlingstein et al., 2023).

Ocean observations indicate that the Southern Ocean (SO) south of 45° S has been accumulating each year about  $0.5 \text{ PgC yr}^{-1}$  since the 1990s (e.g., Takahashi et al., 2009a, b; Lenton et al., 2013; Rödenbeck et al., 2013; Long et al., 2021; Fay et al., 2024; Gray, 2024). Results based on BGC-Argo floats (Southern Ocean Carbon and Climate Observations and Modeling project, SOCCOM) suggest that the CO<sub>2</sub> sink in the SO might be much lower ( $0.16 \text{ PgC yr}^{-1}$  south of 44° S for the period 2015–2017; Gray et al., 2018; Bushinsky et al., 2019), but there is an ongoing debate on the size of the carbon sink in this region depending the periods and methods (Long et al., 2021; Sutton et al., 2021; Hauck et al., 2023b; Gray, 2024). It is also well established that the CO<sub>2</sub> sink in the SO undergoes substantial decadal variability first documented for the 1990s (Le Quéré et al., 2007; Metzl, 2009; Lenton et al., 2013) and subsequently identified for the period 1982–2018 (Landschützer et al., 2015; Kepler and Landschützer, 2019; Mackay et al., 2022; Hauck et al., 2023a, b). However as for the mean state, there are also uncertainties on both the magnitude and phasing of decadal variability in the SO carbon sink mainly due to insufficient sampling (Gloege et al., 2021; Hauck et al., 2023a, b). A recent extension of the period to 1957–2020 suggests that the inter-annual to decadal variability of the SO CO<sub>2</sub> sink was most pronounced after the 1980s (Rödenbeck et al., 2022; Bennington et al., 2022). Whatever the variability of the SO CO<sub>2</sub> sink since the 1960s, the ocean continuously absorbs atmospheric CO<sub>2</sub>, and the distribution of anthropogenic CO<sub>2</sub> ( $C_{\text{ant}}$ ) in the SO is now relatively well documented (e.g., Pardo et al., 2014; Gruber et al., 2019a) thanks to the Global Ocean Data Analysis Project (GLODAP) data synthesis effort for the global ocean (Olsen et al., 2016, 2019, 2020). The SO takes up about 40 % of the total anthropogenic carbon that enters the ocean (Khatiwala et al., 2013; Gruber et al., 2019a).

The anthropogenic CO<sub>2</sub> uptake in the ocean results in lowering carbonate ion concentrations and pH, a chemical process termed “ocean acidification” (OA) (Caldeira and Wickett 2003; Doney et al., 2009). This decreases the saturation state with respect to carbonate minerals (aragonite,  $\Omega_{\text{Ar}}$ , and calcite,  $\Omega_{\text{Ca}}$ ), a process most pronounced in the cold waters at high latitudes where the saturation state is naturally low (Orr et al., 2005; Takahashi et al., 2014; Jiang et al., 2015). The first estimate of  $C_{\text{ant}}$  distribution in the global ocean (for a nominal year 1994; Sabine et al., 2004) shows that the accumulation of  $C_{\text{ant}}$  led to an upward migration of the  $\Omega_{\text{Ar}}$  and  $\Omega_{\text{Ca}}$  saturation horizon in all ocean basins (Feely et al., 2004). This change is particularly pronounced south of the polar front (PF) in the SO due to both  $C_{\text{ant}}$  uptake and the enhanced upwelling of carbon-rich deep waters (e.g., Hauck et

al., 2010; Pardo et al., 2017). It has been suggested, through numerical studies, that depending on future CO<sub>2</sub> emission levels, surface waters in the SO could reach undersaturation state for aragonite by 2030–2050 (Orr et al., 2005; Gangstø et al., 2008; McNeil and Matear, 2008; Negrete-Garcia et al., 2019). Such a change would have multiple and detrimental impacts on marine ecosystems (Fabry et al., 2008; Doney et al., 2012; Bopp et al., 2013), in particular calcifying marine organisms, especially aragonite producers such as pteropods (Hunt et al., 2008; Gardner et al., 2023), as well as calcite-producing planktonic foraminifera (Moy et al., 2009), coccolithophorids (Beaufort et al., 2011), and non-calcifying species such as the abundant SO diatoms (e.g., Benoiston et al., 2017; Petrou et al., 2019; Weir et al., 2020; Duncan et al., 2022) and krill (Kawaguchi et al., 2013).

Hindcast simulations with global ocean biogeochemical models (GOBMs), as well as projections with Earth system models (ESMs), have been used to evaluate the ocean carbon cycle over the past decades and future changes in  $C_{\text{ant}}$  storage, ocean acidification, or impacts of global changes on marine ecosystems. However, current model-based estimates of the contemporary SO CO<sub>2</sub> sink are subject to relatively large uncertainties (e.g., Long et al., 2013; Gooya et al., 2023; Hauck et al., 2020, 2023a, b; Mayot et al., 2023; DeVries et al., 2023). Differences between GOBMs can reach up to  $0.7 \text{ PgC yr}^{-1}$  in the SO (Hauck et al., 2020), which is roughly equivalent to the mean climatological flux of  $0.5 \text{ PgC yr}^{-1}$  (McNeil et al., 2007; Takahashi et al., 2009a, b; Lenton et al., 2013). At the high latitudes of the SO (> 50° S) for the 2010s, ESMs from the Coupled Model Intercomparison Project Phase 6 (CMIP6) simulated either a large sink or a modest source of CO<sub>2</sub> (McKinley et al., 2023). This is mainly due to incorrect or missing physical and/or biological processes in the models (e.g., Pilcher et al., 2015; Kessler and Tjiputra, 2016; Mongwe et al., 2018; Lerner et al., 2021), leading to biases in the seasonality of temperature, dissolved inorganic carbon  $C_{\text{T}}$ , partial pressure of CO<sub>2</sub> ( $p\text{CO}_2$ ), air–sea CO<sub>2</sub> fluxes, pH, or  $\Omega$  (e.g., McNeil and Sasse, 2016; Rodgers et al., 2023; Rustogi et al., 2023; Joos et al., 2023). Such model imperfections should be resolved to gain reliability in future projections of CO<sub>2</sub> uptake, OA, productivity, and the responses of the marine ecosystems (Frölicher et al., 2015; Hauck et al., 2015; Sasse et al., 2015; Kessler and Tjiputra, 2016; McNeil and Sasse 2016; Kwiatkowski and Orr, 2018; Negrete-Garcia et al., 2019; Burger et al., 2020; Krumhardt et al., 2022; Jiang et al., 2023; Mongwe et al., 2024). In this context, long-term biogeochemical observations are particularly valuable to quantify and understand recent past and current changes, and ultimately evaluate model simulations, as often concluded in modeling studies (e.g., Kessler and Tjiputra, 2016; Gooya et al., 2023; Wright et al., 2023; Hauck et al., 2023a; Mayot et al., 2023; Rodgers et al., 2023).

Although the SO south of the polar front remains much less observed than other oceanic regions, several observations-based studies have estimated the decrease in

**Table 1.** Trends of oceanic  $f\text{CO}_2$  ( $\mu\text{atm yr}^{-1}$ ) and pH (per decade) in the Southern Ocean south of the polar front based on observations. IO: Indian Ocean sector. PO: Pacific Ocean sector. AO: Atlantic Ocean sector. SO SPSS: Southern Ocean subpolar seasonally stratified biome (around 50–60° S). PZ: polar zone. NR: not reported. Standard deviations when available are given in brackets.

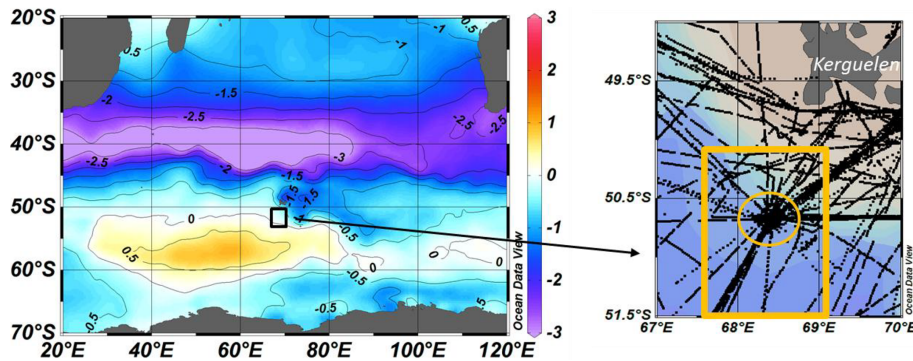
Period	Season	Zone	Trend $f\text{CO}_2$ $\mu\text{atm yr}^{-1}$	Trend pH per decade	Reference
1991–2000	Summer	IO PZ 55–60° S	2.93	−0.035	Xue et al. (2018)
2001–2011	Summer	IO PZ 55–60° S	1.41	−0.016	Xue et al. (2018)
2005–2019	Summer	IO PZ 54–64° S	NR	−0.026 (0.003)	Brandon et al. (2022)
1998–2019	Summer	IO 50° S–68° E	1.9 (0.3)	−0.019 (0.004)	Leseurre et al. (2022)
1998–2019	Summer	IO 55° S–63° E	2.1 (0.3)	−0.022 (0.003)	Leseurre et al. (2022)
1998–2007	Summer	IO 55° S–63° E	5.3 (0.4)	−0.050 (0.016)	Leseurre et al. (2022)
2006–2019	Summer	IO 55° S–63° E	0.3 (0.2)	No trend	Leseurre et al. (2022)
1969–2003	Summer	PO 55–62° S	1.7 (0.2)	−0.020 (0.003)	Midorikawa (2012)
2002–2012	Annual	Drake North	2.21 (0.55)	−0.023 (0.007)	Takahashi et al. (2014)
2002–2012	Annual	Drake South	1.50 (0.65)	−0.015 (0.008)	Takahashi et al. (2014)
2002–2015	Summer	Drake North	1.95 (0.55)	−0.021 (0.006)	Munro et al. (2015)
2002–2015	Winter	Drake North	1.92 (0.24)	−0.018 (0.003)	Munro et al. (2015)
2002–2015	Summer	Drake South	1.30 (0.85)	−0.017 (0.010)	Munro et al. (2015)
2002–2015	Winter	Drake South	0.67 (0.39)	−0.008 (0.004)	Munro et al. (2015)
2002–2015	Annual	Drake North	1.74 (0.15)	−0.019 (0.002)	Munro et al. (2015)
2002–2015	Annual	Drake South	1.16 (0.27)	−0.015 (0.003)	Munro et al. (2015)
1981–2011	Annual	SO SPSS	1.44 (0.10)	−0.020 (0.002)	Lauvset et al. (2015)
1991–2011	Annual	SO SPSS	1.46 (0.11)	−0.021 (0.002)	Lauvset et al. (2015)
1993–2018	Annual	SO 44–75° S	NR	−0.0165 (0.0001)	Iida et al. (2021)

pH in surface waters in response to the increase in oceanic  $\text{CO}_2$  fugacity,  $f\text{CO}_2$  (Midorikawa et al., 2012; Takahashi et al., 2014; Lauvset et al., 2015; Munro et al., 2015; Xue et al., 2018; Iida et al., 2021; Leseurre et al., 2022; Brandon et al., 2022). Results showed a large range in the pH trends from −0.008 −0.035 per decade depending on the period and the region of interest. Most of these analyses were based on summer observations (Table 1), and some studies highlighted contrasting pH trends on a 5–10-year timescale probably linked to large-scale climate variability such as the Southern Annular Mode (SAM) (e.g., Xue et al., 2018). Given such variability, it is important to continue monitoring  $f\text{CO}_2$  and pH trends and, if possible, at different seasons as future change in  $\text{CO}_2$  uptake and potential tipping points of the carbonate saturation state also depend on seasonality (Sasse et al., 2015). The above observational studies were dedicated to pH changes in surface waters. In contrast to northern high latitudes (e.g., Olafsson et al., 2009, 2010; Franco et al., 2021; Skjelvan et al., 2022), few studies in the SO evaluated decadal changes of carbonate system properties and acidification in the water column based on time-series stations. These changes in the SO water column were investigated from data collected during cruises generally 3 to 15 years apart (e.g., Hauck et al., 2010; Van Heuven et al., 2011; Pardo et al., 2017; Tanhua et al., 2017; Carter et al., 2019).

The present study complements in time, seasons, and in the water column the surface  $f\text{CO}_2$  and pH trends inves-

tigated by Leseurre et al. (2022) in different regions of the southern Indian Ocean for the period 1998–2019 during austral summer. South of the PF around 50° S, Leseurre et al. (2022) showed that in summer the surface  $f\text{CO}_2$  increase and pH decrease over 20 years were mainly driven by the accumulation of anthropogenic  $\text{CO}_2$  by about  $+0.6 \pm 0.2 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$  and by a small warming of  $+0.03 \pm 0.02 \text{ }^\circ\text{C yr}^{-1}$ . In addition Leseurre et al. (2022) showed that in the recent decade, 2007–2019, the  $f\text{CO}_2$  trend was low ( $+0.3 \pm 0.2 \mu\text{atm yr}^{-1}$ ) compared to the previous decade ( $+5.3 \pm 0.4 \mu\text{atm yr}^{-1}$  over 1998–2007), highlighting the sensitivity of the  $f\text{CO}_2$  and pH trends to the selected time period (especially during summer). In particular, they observed relatively stable pH values over 2010–2019 (i.e., no decrease in pH) with no clear explanation on the origin of the slow-down of the  $f\text{CO}_2$  and pH trends in surface waters south of the PF in recent years. To complement the analysis by Leseurre et al. (2022) based on summer observations over the period 1998–2019, this study focuses on one location regularly visited south of the polar front (around 50° S–68° E southwest of Kerguelen Island; Fig. 1). The analysis period is first extended back to 1985 and forward to 2021 to investigate the recent status of  $f\text{CO}_2$  and pH. We also evaluate the trends during late winter using sparse data in October/November. The combination of in situ observations and monthly estimates from a neural network model over the period 1985–2020 (Chau et al., 2022) enables us to assess potential changes in seasonality of the surface ocean carbon-





**Figure 1.** Left: annual air–sea  $\text{CO}_2$  flux ( $\text{molC m}^{-2} \text{yr}^{-1}$ ) in the southern Indian Ocean for year 2020 from the FFNN model (negative flux for ocean sink, positive flux for ocean source). The black box identifies the location of the study southwest of Kerguelen Islands. Right: track of cruises with underway  $f\text{CO}_2$  data southwest of Kerguelen Islands. The station at  $50^\circ 40' \text{S}$ – $68^\circ 25' \text{E}$  occupied in 1985, 1992–1993, and 1998–2021 is indicated by a yellow circle. The yellow square is the region selected to calculate the mean values from the underway surface observations and from the FFNN model. Figures produced with Ocean Data View (ODV; Schlitzer, 2018).

ate system (including  $f\text{CO}_2$ ,  $C_T$ , pH,  $\Omega$ ) as suggested in recent decades or in future scenarios (Hauck and Völker, 2015; Gallego et al., 2018; Landschützer et al., 2018; Kwiatkowski and Orr, 2018; Kwiatkowski et al., 2020; Lerner et al., 2021; Fassbender et al., 2022; Yun et al., 2022; Rodgers et al., 2023; Joos et al., 2023). The changes observed in surface waters will be related to changes in  $C_{\text{ant}}$  concentrations estimated in the water column and will be complemented by an analysis of OA at depth between 1985 and 2021. Finally we will explore the long-term change of surface  $f\text{CO}_2$  and pH since the 1960s and potential future changes of the carbonate system at this time-series site.

## 2 Data selection, methods, and quality control

### 2.1 Study area and data selection

This study focuses on a high-nutrient low-chlorophyll area (HNLC; Minas and Minas, 1992) in the Indian sector of the Southern Ocean (SO) in the Permanent Open-Ocean Zone (POOZ) south of the polar front (PF) and southwest of Kerguelen Islands (around  $50^\circ \text{S}$ – $68^\circ \text{E}$ , Fig. 1). The Kerguelen Plateau is an extended topographic feature that controls part of the Antarctic Circumpolar Current (ACC) and generates eddies (Daniault and Ménard, 1985) and the northward deflection of the PF just east of the island (Pauthenet et al., 2018). The plateau is also a region of relatively high chlorophyll-*a* (Chl-*a*) concentration (Moore and Abbott, 2000; Mongin et al., 2008) and strong  $\text{CO}_2$  uptake during austral spring–summer that contrasts with the weaker sink over the POOZ/HNLC (Metzl et al., 2006; Jouandet et al., 2008, 2011; Lo Monaco et al., 2014; Leseurre et al., 2022). The POOZ/HNLC region west (upstream) of the Kerguelen Plateau is characterized by rather stable water mass properties (temperature, salinity, oxygen, or nutrients) over time and low eddy activity compared to the plateau (Daniault

and Ménard, 1985; Chapman et al., 2015; Dove et al., 2022). In this region, located in the deep Enderby Basin, the flow is not constrained by topography and there is no local upwelling that would import  $C_T$ -rich waters to the surface layers as observed on the eastern side of the Kerguelen Plateau (Brady et al., 2021).

The Indian sector of the SO is also recognized to host the strongest winds in the SO leading to year-round high gas transfer coefficients (Wanninkhof and Trinanes, 2017). As a result, and in contrast to the Atlantic sector of the SO, the Indian region south of  $45^\circ \text{S}$  was a periodic annual  $\text{CO}_2$  source, especially in the 1960s to the 1980s (Rödenbeck et al., 2022; Bennington et al., 2022; Prend et al., 2022; Gray, 2024). In the POOZ–HNLC region, high winter wind speed (monthly average up to  $16 \text{ m s}^{-1}$ ) and associated heat loss drive deep mixing. Deep winter mixing entrains subsurface properties to the surface layer and increases surface  $C_T$  concentrations, leading to wintertime outgassing of  $\text{CO}_2$  (Metzl et al., 2006). This combination of characteristics makes the region an ideal test bed for 1-D modeling studies investigating the temporal dynamics and drivers of biogeochemical processes including nutrients, iron, phytoplankton, and carbon (Pondaven et al., 1998, 2000; Louanchi et al., 1999, 2001; Jabaud-Jan et al., 2004; Metzl et al., 2006; Mongin et al., 2006, 2007; Kane et al., 2011; Pasquer et al., 2015; Demuynck et al., 2020).

Here we used surface and water column observations around location  $50^\circ 40' \text{S}$ – $68^\circ 25' \text{E}$  (Fig. 1, Table S1 in the Supplement), historically called KERFIX station (Kerguelen FIXed station) sampled from 1990 to 1995 in the framework of the WOCE and JGOFS programs (Jeandel et al., 1998). The station was first occupied in March 1985 during the INDIGO-1 cruise (Indian Ocean Geochemistry; Poisson, 1985; Poisson et al., 1988), and since 1998 it has been regularly visited during the OISO cruises (Océan Indien Service d’Observations; Metzl and Lo Monaco, 1998, <https://doi.org/10.18142/228>). The regular occupation from

1985 to 2021 makes it the longest time-series station in the Southern Ocean POOZ/HNLC area for investigating the inter-annual to decadal trends of carbonate properties in surface waters and across the water column (0–1600 m). Despite the occasional large anomalies in surface waters properties (e.g., lower temperature in December 1998, lower salinity in February 2013), we consider all observations selected for this study both in surface waters and the water column to be representative of the water masses in this POOZ/HNLC region upstream of the Kerguelen Plateau.

Data for the period 1985–2011 were extracted from the GLODAP data product, version V2.2021 (Lauvset et al., 2021a, b; Table S1a). Observations collected during OISO cruises from 2012 to 2021 will be included in GLODAP-V3. For the surface water properties, all available underway  $f\text{CO}_2$  data were selected (Fig. 1). This includes one cruise in November 1962 (Keeling and Waterman, 1968) and 41 cruises from 1991 to 2021 (Table S1b). All surface temperature, salinity, and  $f\text{CO}_2$  data were extracted from the SOCAT (Surface Ocean  $\text{CO}_2$  Atlas) data-product version v2022 (Bakker et al., 2016, 2022) and have an accuracy of  $f\text{CO}_2$  between 2 and 5  $\mu\text{atm}$ .

## 2.2 Methods

The methods for surface underway  $f\text{CO}_2$  and biogeochemical properties (oxygen,  $C_T$ , total alkalinity  $A_T$ , nutrients) in the water column for the INDIGO-1, KERFIX, and OISO cruises were described in previous studies (e.g., Poisson et al., 1993; Louanchi et al., 2001; Metzl et al., 2006; Metzl, 2009; Mahieu et al., 2020; Leseurre et al., 2022). Here we briefly recall the methods for underway  $f\text{CO}_2$  and water column observations.

### 2.2.1 Surface $f\text{CO}_2$ data

For  $f\text{CO}_2$  measurements in 1991–2021, sea-surface water was continuously equilibrated with a “thin film” type equilibrator thermostated with surface seawater (Poisson et al., 1993). The  $x\text{CO}_2$  in the dried gas was measured with a non-dispersive infrared analyzer (NDIR, Siemens UL-TRAMAT 5F or 6F). Standard gases for calibration (around 270, 350, and 490 ppm) were measured every 6 h. To correct  $x\text{CO}_2$  dry measurements to  $f\text{CO}_2$  in situ data, we used polynomials from Weiss and Price (1980) for vapor pressure and from Copin-Montégut (1988, 1989) for temperature. Note that when incorporated in the SOCAT database, the original  $f\text{CO}_2$  data are recomputed (Pfeil et al., 2013) using temperature correction from Takahashi et al. (1993). Given the small difference between equilibrium temperature and sea surface temperature ( $+0.56 \pm 0.30$  °C on average for the cruises in 1998–2021), the  $f\text{CO}_2$  data from SOCAT used in this analysis (Bakker et al., 2022) are almost identical (within 1  $\mu\text{atm}$ ) to the original  $f\text{CO}_2$  values from our cruises (<http://www.ncei.noaa.gov/access/ocean-carbon-data-system/>

[oceans/VOS\\_Program/OISO.html](https://www.ncei.noaa.gov/access/ocean-carbon-data-system/oceans/VOS_Program/OISO.html), last access: 15 January 2024).

### 2.2.2 Water column data

Over the period 1990–1995, water samples were collected during the KERFIX program on the ship *La Curieuse* at standard depths using 8 L Niskin bottles mounted on a stainless-steel cable and equipped with reversing SIS pressure and temperature probes. Methods and accuracy for the geochemical measurements used in this analysis ( $A_T$ ,  $C_T$ , oxygen, nutrients) are detailed by Jeandel et al. (1998) and by Louanchi et al. (2001). From 1998 onwards, the station was occupied within the framework of the OISO long-term monitoring program on board the R/V *Marion Dufresne*. We used conductivity–temperature–depth (CTD) sensors mounted on 24 rosette samplers equipped with 12 L Niskin bottles. Temperature and salinity measurements have an accuracy of 0.002 °C and 0.005 respectively (Mahieu et al., 2020). Samples for  $A_T$  and  $C_T$  were filled in 500 mL glass bottles and poisoned with 300  $\mu\text{L}$  of saturated mercuric chloride solution to halt biological activity. Discrete  $C_T$  and  $A_T$  samples were analyzed onboard by potentiometric titration derived from the method developed by Edmond (1970) using a closed cell. Based on replicate samples from the surface or depth, the repeatability for  $A_T$  and  $C_T$  varies from 1 to 3.5  $\mu\text{mol kg}^{-1}$  depending on the cruise. The accuracy of  $\pm 3$   $\mu\text{mol kg}^{-1}$  was ensured by daily analyses of certified reference materials (CRMs) provided by Andrew Dickson’s laboratory (Scripps Institute of Oceanography).

Dissolved oxygen ( $\text{O}_2$ ) concentration was determined by a sensor fixed on the rosette, and values were adjusted based on discrete measurements (Winkler method, Carpenter, 1965) using a potentiometric titration system. Accuracy for  $\text{O}_2$  is  $\pm 2$   $\mu\text{mol kg}^{-1}$  (Mahieu et al., 2020). Although long-term deoxygenation in the Southern Ocean has been suggested (Ito et al., 2017; Schmidtko et al., 2017; Oschlies et al., 2018), no significant trend in  $\text{O}_2$  was identified over 1985–2021 at this station around 50° S in both the surface and the subsurface layer (at the depth of the temperature minimum representing winter water, a layer used for  $C_{\text{ant}}$  calculations as described later). However, in the station data a small  $\text{O}_2$  decrease was detected around 800 m in the  $\text{O}_2$  minimum layer over 36 years ( $-0.22 \pm 0.07$   $\mu\text{mol kg}^{-1} \text{yr}^{-1}$ ). As this has no impact on the interpretation for pH and  $\Omega$  trends for this analysis, the observed change of  $\text{O}_2$  at depth will not be discussed further. Here the  $\text{O}_2$  data are mainly used for the calculation of anthropogenic  $\text{CO}_2$  concentrations, and the observed  $\text{O}_2$  change at depth is too small to have an impact on temporal variations of  $C_{\text{ant}}$  concentrations given the uncertainty of the calculation.

Nitrate ( $\text{NO}_3$ ) and silicate (DSi) were analyzed on board or at LOCEAN/Paris by colorimetry following the methods described by Tréguer and Le Corre (1975) for 1998–2008 or from Coverly et al. (2009) for 2009–2021. The uncertainty

of  $\text{NO}_3$  and  $\text{DSi}$  measurements is  $\pm 0.1 \mu\text{mol kg}^{-1}$ . Based on replicate measurements on deep samples, we estimate an error of about 0.3 % for both nutrients. Phosphate ( $\text{PO}_4$ ) samples were analyzed from a few cruises following the method of Murphy and Riley (1962) revised by Strickland and Parsons (1972) with an uncertainty of  $\pm 0.02 \mu\text{mol kg}^{-1}$ . When nutrient data are not available for a cruise, we used climatological values based on the seasonal nutrient cycles inferred from data from 1990 to 2021. This method has a very small impact on the carbonate system calculations and the trend analysis as we did not detect any significant trends in nutrients in surface or at depth since 1985 (not shown) as opposed to what has been observed at higher latitudes of the SO (Iida et al., 2013; Hoppema et al., 2015). However, we will see in Sect. 3.1 that the inter-annual variability of nutrients (especially  $\text{DSi}$  in the HNLC region) might inform on potential changes in biological processes.

Samples were collected in the top layers (0–150 m) for chlorophyll *a* (Chl *a*). For that, 1–2 L of seawater was filtered onto  $0.7 \mu\text{m}$  glass microfiber filters (GF/F, Whatman), and filters were stored at  $-80^\circ\text{C}$  onboard. Back at the LOCEAN/Paris laboratory, samples were extracted in 90 % acetone (Strickland and Parsons, 1972), and the fluorescence of Chl *a* was measured on a Turner Type 450 fluorometer for the period 1998–2007 and since 2009 at 670 nm on a Hitachi F-4500 spectrofluorometer (Neveux and Lantoiné, 1993).

### 2.2.3 Data quality control and data consistency

When exploring the trends of ocean properties based on different cruises more than 35 years apart, it is important to first verify the consistency of the data and to correct for any bias or drift. The INDIGO data from 1985 (i.e., prior to CRMs available for  $A_T$  and  $C_T$ ) were first controlled prior to their incorporation into the original GLODAP product (Sabine et al., 1999; Key et al., 2004), and corrections for  $A_T$  and  $C_T$  were revisited within the framework of the CARINA project (CARbon IN the Atlantic; Lo Monaco et al., 2010) and the GLODAPv2 synthesis (Olsen et al., 2016). A secondary quality control was performed on the data from the OISO cruises collected between 1998 and 2011 within the CARINA and GLODAP-v2 initiatives (Lo Monaco et al., 2010; Olsen et al., 2016). Significant offsets were identified for  $A_T$  and  $C_T$  in samples from the KERFIX cruises (1990–1993) compared to INDIGO and OISO data, and it was proposed to correct the original values by  $-35 \mu\text{mol kg}^{-1}$  for  $C_T$  and  $-49 \mu\text{mol kg}^{-1}$  for  $A_T$  (Metzl et al., 2006). These corrections were applied in GLODAP version v2.2019 (Olsen et al., 2019) and resulted in coherent  $A_T$  and  $C_T$  concentrations for KERFIX in the deep layers compared to other cruises (Supplement Table S2, Fig. S1). The same data quality control protocol as for GLODAP-v2 was applied to data from OISO cruises for the period 2012–2021 (Mahieu et al., 2020). Given the accuracy of the data no systematic bias (except in 2014) was found for the properties measured in 2012–2021.

The time series of  $A_T$  and  $C_T$  at depths below 1450 m for all cruises in 1985–2021 show some variability but no trend over 36 years as expected in the bottom waters in this region (Fig. S1). However, we identified a small bias for  $C_T$  in 2014 (cruise OISO-23) where  $C_T$  concentrations in the deep water appeared slightly lower ( $2228\text{--}2234 \mu\text{mol kg}^{-1}$  in 2014 compared to the mean value of  $2240.7 \pm 3.7 \mu\text{mol kg}^{-1}$ ; Table S2, Fig. S1). When compared to  $f\text{CO}_2$  in surface waters, we also suspect the  $C_T$  data in the mixed layer in 2014 to be too low by about  $10 \mu\text{mol kg}^{-1}$  (Figs. S2, S3). Therefore we applied a WOCE/GLODAP flag 3 for  $C_T$  data of this cruise and will not use the station data in 2014 for the  $C_{\text{ant}}$  calculations and the trend analysis described in this study.

### 2.2.4 CMEMS-LSCE-FFNN model

As most of the cruises took place during austral summer and data are not available each year, we completed the observations with the results from an ensemble of feed-forward neural network models (CMEMS-LSCE-FFNN or FFNN for simplicity here; Chau et al., 2022). The FFNN model allows mapping at global-scale monthly surface  $f\text{CO}_2$  from the SOCAT gridded datasets and ancillary variables. The reconstructed  $f\text{CO}_2$  is then used to derive monthly surface  $C_T$  and pH fields as well as air–sea  $\text{CO}_2$  fluxes. This data product is used to investigate the trends for different seasons and to derive estimates of annual air–sea  $\text{CO}_2$  fluxes to interpret the change in  $\text{CO}_2$  uptake, if any. For a full description of the model, access to the data, and a statistical evaluation of  $f\text{CO}_2$  reconstructions, please refer to Chau et al. (2022). Within this study, we compared the FFNN  $f\text{CO}_2$  with observations from 35 cruises for the years between 1991 and 2020 (Table S3, Fig. S2a). Except for a few periods (January 1993 and January 2002), model–data differences are generally within  $\pm 10 \mu\text{atm}$  with a mean difference of  $2.1 \pm 7 \mu\text{atm}$  for the 35 co-located periods. Note that, as opposed to sea surface  $f\text{CO}_2$ , no temporal trend was identified for the differences between the observed and reconstructed  $f\text{CO}_2$  (Fig. S2b); i.e., the trends of sea surface  $f\text{CO}_2$  derived from the observations and from the FFNN model should be the same. Aside from the  $f\text{CO}_2$  reconstructions, surface ocean alkalinity ( $A_T$ ) fields are also provided by using the multivariate linear regression model LIAR (Carter et al., 2016, 2018) based on sea surface temperature, salinity, and nutrient concentration.

### 2.2.5 Calculations of carbonate properties

Based on the data available for each cruise ( $f\text{CO}_2$ , or  $A_T$  and  $C_T$ ) or from the FFNN model ( $f\text{CO}_2$  and  $A_T$ ), other carbonate system properties (pH,  $[\text{H}^+]$ ,  $[\text{CO}_3^{2-}]$ , and  $\Omega$ ) were calculated using the CO2sys program (version CO2sys\_v2.5; Orr et al., 2018) developed by Lewis and Wallace (1998) and adapted by Pierrot et al. (2006) with K1 and K2 dissociation constants from Lueker et al. (2000) as recommended (Dick-

son et al., 2007; Orr et al., 2015; Wanninkhof et al., 2015). The total boron concentration was calculated according to Uppström (1974) and  $\text{KSO}_4$  from Dickson (1990). To calculate the properties with the underway surface  $f\text{CO}_2$  dataset, we used the  $A_T$ – $S$  relationship based on  $A_T$  and  $C_T$  data from the OISO cruises over the period 1998–2019 in the southern Indian sector as described by Leseurre et al. (2022):

$$A_T = 64.341 \times S + 106.764 \text{ (rmse} = 7.5 \mu\text{mol kg}^{-1}, n = 4775\text{)}. \quad (1)$$

The use of other  $A_T$ – $S$  relationships (e.g., Millero et al., 1998; Jabaud-Jan et al., 2004; Lee et al., 2006; Carter et al., 2018) would change slightly the  $A_T$  concentrations but neither the  $A_T$  trend nor the interpretation of the  $C_T$ , pH, or  $\Omega$  trends. However, as salinity is an important predictor in the calculation of  $A_T$ ,  $C_T$ , or pH from  $f\text{CO}_2$  data, we have assessed the original underway salinity data and found biases for a few cruises in 1992, 1993, and 1995 (Table S1b). For these cruises or when salinity was not measured, we used the salinity from the World Ocean Atlas (WOA; Antonov et al., 2006) in the SOCAT datasets (Pfeil et al., 2013, identified “WOA” in Table S1b). Monthly  $f\text{CO}_2$  and  $A_T$  data extracted from the CMEMS-LSCE-FFNN datasets at the station location (50.5° S–68.5° E) over 1985–2020 were used to calculate the carbonate properties in the same way as from observations.

### 2.2.6 Comparisons of different datasets and the FFNN model

To validate the properties calculated using the  $f\text{CO}_2$  data for 1991–2021 or from the FFNN model over 1985–2020, we compared the calculated values ( $A_T$ ,  $C_T$ , pH,  $[\text{H}^+]$ ,  $[\text{CO}_3^{2-}]$ ,  $\Omega$ ) with those calculated from  $A_T$  and  $C_T$  data measured in the mixed layer at the OISO-KERFIX station occupied in 1985 and between 1993 and 2021. For this comparison, we averaged the continuous underway  $f\text{CO}_2$  data selected in a box around the station location (50–51.5° S, 67.5–69° E; yellow box in Fig. 1). Results of the comparisons between various datasets are detailed in the Supplement (Tables S3 and S4). During the period 1993–2021, there are 22 station occupations with co-located underway  $f\text{CO}_2$  data for different seasons (but mainly in summer). Since we found a close agreement between measured  $f\text{CO}_2$  and the FFNN model (Table S3, Fig. S2), mismatches in all calculated carbonate system properties between the underway  $f\text{CO}_2$  dataset and the FFNN model are small, falling within the range of the errors associated with the calculations (Orr et al., 2018). For example, for 35 co-located periods, the mean differences in calculated  $C_T$  of  $1.5 \pm 5 \mu\text{mol kg}^{-1}$  or pH of  $-0.002 \pm 0.008$  are in the range of the theoretical error of about  $5 \mu\text{mol kg}^{-1}$  and 0.007 respectively when taking into account measurements errors on salinity, temperature, nutrients,  $f\text{CO}_2$ , and  $A_T$  (Orr et al., 2018). On the other hand, compared to the

station data in the mixed layer (Table S4), the calculated  $A_T$  using Eq. (1) is slightly higher by about  $5 \mu\text{mol kg}^{-1}$ . This explains the relatively high differences for  $C_T$  (mean difference around  $8 \mu\text{mol kg}^{-1}$ ) and for pH (mean difference around 0.008) calculated with  $f\text{CO}_2$  and the  $A_T$ – $S$  relationship. The differences of calculated values with observations are, on average, in the range of uncertainties of the carbonate system calculations using  $A_T$ – $C_T$  pairs (error for  $f\text{CO}_2$  around  $13 \mu\text{atm}$  and for pH around 0.0144). Importantly, there is no temporal trend for the differences between calculated and observed properties (Fig. S3b). We are thus confident using the selected  $f\text{CO}_2$  data for the trend analysis presented in this study. The independent comparison with  $A_T$  and  $C_T$  measurements in the mixed layer also indicates that the FFNN model results for  $A_T$  and  $C_T$  are close to the observations (Tables S4, S5, Fig. S4) as well as for calculated pH,  $[\text{H}^+]$ ,  $[\text{CO}_3^{2-}]$ ,  $\Omega_{\text{Ca}}$ , and  $\Omega_{\text{Ar}}$ . This somehow validates the use of the FFNN data for the trend analysis over the period 1985–2020 and for different seasons, although the FFNN model was not constrained by in situ  $f\text{CO}_2$  before 1991, few data in austral winter since 1991, and no Chl-*a* satellite data available before 1998. Nevertheless, the model shows a good agreement with observations collected in March 1985 (Table S5, Fig. S4).

## 3 Results and discussion

### 3.1 Variability and trend of sea surface $f\text{CO}_2$ and air–sea $\text{CO}_2$ fluxes: 1985–2021

The  $f\text{CO}_2$  observations around 50° S–68° E and their mean values for each cruise are shown in Fig. 2a.  $f\text{CO}_2$  measurements are available for different seasons since 1991, though most of them stem from austral summer (January–February). During austral summer, the ocean  $f\text{CO}_2$  was generally lower than in the atmosphere (i.e., the ocean was a  $\text{CO}_2$  sink), whereas from July to October it was near equilibrium. The same seasonal change is obtained from the FFNN model for the period 1991–2020 (Fig. 2a). The model also indicates that between 1985 and the mid-1990s the  $f\text{CO}_2$  during austral winter (May–September) was always higher than the atmospheric  $f\text{CO}_2$ , leading to an annual  $\text{CO}_2$  source during this period (Fig. 3). In 1985 the oceanic  $f\text{CO}_2$  from the FFNN model was higher than in the atmosphere from March to October (Fig. S4), resulting in an annual  $\text{CO}_2$  source of  $+0.8 \text{ molC m}^{-2} \text{ yr}^{-1}$ . The model estimates a decrease of the annual  $\text{CO}_2$  source until the end of the 1990s followed by an increase of the source over the following decade (Fig. 3). Around the year 2010, the annual  $\text{CO}_2$  flux was around  $+0.5 \text{ molC m}^{-2} \text{ yr}^{-1}$  and then decreased over the last decade to change into an annual  $\text{CO}_2$  sink that increased to reach  $-0.5 \text{ molC m}^{-2} \text{ yr}^{-1}$  in 2020. For this reason and given the data available since 1991, we evaluated the summer and winter trends in  $f\text{CO}_2$ ,  $C_T$ , and pH from the FFNN model over

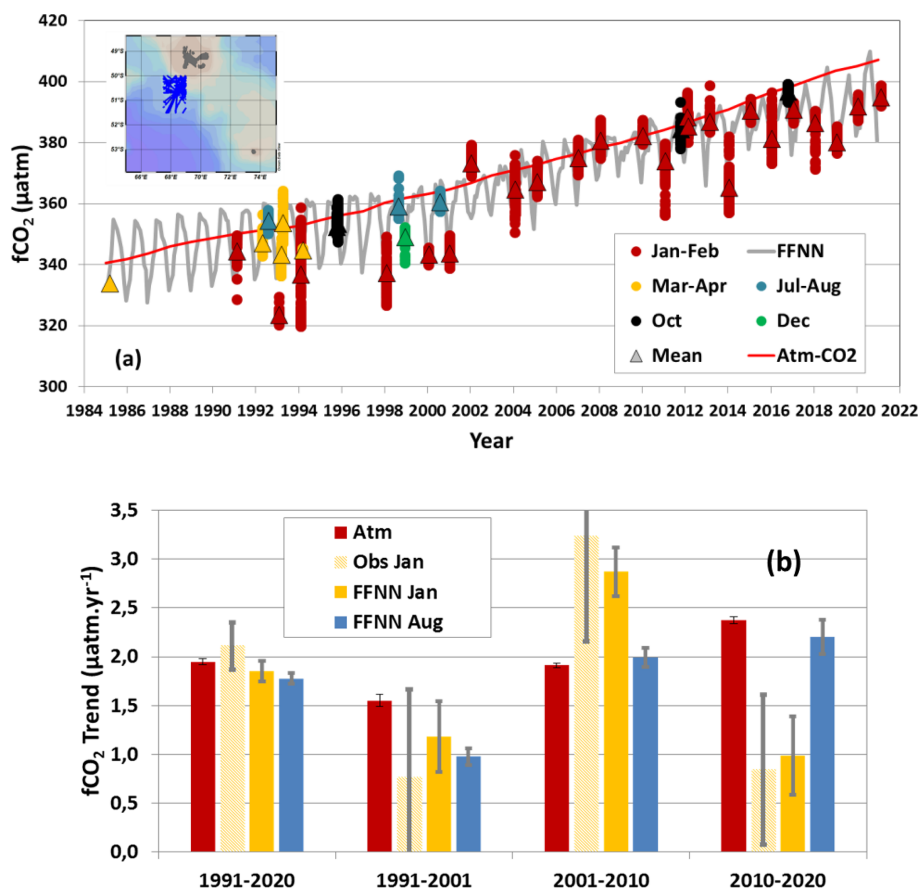
**Table 2.** Trends of oceanic  $f\text{CO}_2$  ( $\mu\text{atm yr}^{-1}$ ), pH total scale (TS per decade), and  $C_T$  ( $\mu\text{mol kg}^{-1} \text{yr}^{-1}$ ) at the OISO-KERFIX location ( $50^\circ 40' \text{S} - 68^\circ 25' \text{E}$ ) in the southern Indian Ocean for different periods based on observations (Obs.) and the FFNN model (FFNN). Standard deviations are given in brackets.

Period	Season	Trend $f\text{CO}_2$ $\mu\text{atm yr}^{-1}$	Trend pH TS per decade	Trend $C_T$ $\mu\text{mol kg}^{-1} \text{yr}^{-1}$	
1962–2016	November	1.31 (0.32)	−0.014 (0.002)	0.47 (0.01)	Obs.
1991–2021	Summer	2.10 (0.22)	−0.022 (0.002)	0.57 (0.16)	Obs.
1991–2001	Summer	0.76 (0.90)	−0.009 (0.010)	0.05 (0.64)	Obs.
2001–2010	Summer	3.23 (1.07)	−0.035 (0.011)	1.03 (0.77)	Obs.
2010–2020	Summer	0.84 (0.77)	−0.008 (0.008)	0.70 (0.68)	Obs.
1985–2020	Summer	1.71 (0.08)	−0.018 (0.001)	0.68 (0.05)	FFNN
1991–2020	Summer	1.85 (0.11)	−0.020 (0.001)	0.68 (0.07)	FFNN
1991–2001	Summer	1.18 (0.26)	−0.013 (0.004)	0.60 (0.30)	FFNN
2001–2010	Summer	2.87 (0.25)	−0.030 (0.003)	1.08 (0.24)	FFNN
2010–2020	Summer	0.98 (0.40)	−0.010 (0.004)	0.38 (0.26)	FFNN
1985–2020	Winter	1.64 (0.05)	−0.017 (0.001)	0.55 (0.04)	FFNN
1991–2020	Winter	1.78 (0.15)	−0.018 (0.001)	0.56 (0.05)	FFNN
1991–2001	Winter	0.98 (0.09)	−0.010 (0.001)	0.18 (0.14)	FFNN
2001–2010	Winter	1.99 (0.10)	−0.021 (0.001)	1.02 (0.12)	FFNN
2010–2020	Winter	2.21 (0.17)	−0.022 (0.002)	0.69 (0.30)	FFNN
1985–2020	Annual	1.57 (0.03)	−0.0165 (0.0004)	0.58 (0.05)	FFNN

the three periods 1991–2001, 2001–2010, and 2010–2020 and compared the summer trends with those deduced from observations (Table 2). The analysis of trends and their associated drivers for different seasons and periods will allow us to explore links with the variability of primary production and/or the Southern Annual Mode (SAM). Shifts from a negative to a positive SAM index (Fig. 3) may have strengthened the upwelling of deep waters and could therefore impact ocean properties throughout the water column including  $C_T$ , nutrients, primary production, or pH (e.g., Lovenduski and Gruber, 2005; Lenton et al., 2009; Hauck et al., 2013; Hoppema et al., 2015; Pardo et al., 2017).

From the first underway measurements obtained at the OISO-KERFIX site in February 2021 to the last measurements used in this study in February 1991, the average oceanic  $f\text{CO}_2$  increased by  $+50.5 \mu\text{atm}$  (from  $344.4 \pm 1.5$  to  $394.9 \pm 1.5 \mu\text{atm}$ ; Fig. 2a). During the same period, the atmospheric  $\text{CO}_2$  increased by  $57 \mu\text{atm}$  in this region (recorded at the Crozet Islands; Dlugokencky and Tans, 2022). This first comparison of two cruises 30 years apart indicates that the oceanic  $f\text{CO}_2$  increase was close to that of the atmosphere. During the same period, we observed small variations in  $A_T$  (average  $A_T = 2276.5 \pm 4.5 \mu\text{mol kg}^{-1}$ ) and a clear increase in  $C_T$  (Figs. 4a and S5). This suggests that most of the change observed in oceanic  $f\text{CO}_2$  and  $C_T$  over the last 30 years is due to the uptake of anthropogenic  $\text{CO}_2$ . However, the evolution of air–sea  $\text{CO}_2$  fluxes (Fig. 3) suggests that other mechanisms were at play over shorter periods, and changes in the air–sea  $f\text{CO}_2$  disequilibrium (Fig. 2a) suggest that different drivers may be involved in summer and in winter.

Summer data are characterized by a strong inter-annual variability in both  $f\text{CO}_2$  and  $C_T$  (Figs. 2a and 4a) with the ocean being a  $\text{CO}_2$  source in January 2002, but a strong sink in January 1993, 1998, 2014, 2016, and 2019. In January 1998, when the surface ocean experienced a warm anomaly (Jabaud-Jan et al., 2004), the low  $f\text{CO}_2$  of  $337 \mu\text{atm}$  and the low  $C_T$  of  $2110 \mu\text{mol kg}^{-1}$  (Figs. 4a and S5) co-occurred with intense primary production (Fig. 5), probably supported by diatoms as suggested by very low DSi concentrations ( $< 2 \mu\text{mol kg}^{-1}$  down to 100 m, Fig. S6). In January 2014 and 2016, mixed-layer DSi concentrations were also remarkably small ( $< 5 \mu\text{mol kg}^{-1}$  down to 75 m; Fig. S6). In 2014 low DSi coincided with Chl-*a* levels that started to increase in mid-November 2013 and stayed at a high level until February 2014 (surface Chl *a*  $> 0.3 \text{ mg m}^{-3}$ ; Figs. 5 and S7). The intense primary production contributed to the low  $f\text{CO}_2$  of  $365 \mu\text{atm}$  reached by mid-January 2014, a value as low as 10 years earlier (Fig. 2a). To the contrary, in 2002 relatively low Chl *a* (mean Chl *a*  $< 0.2 \text{ mg m}^{-3}$ ; Fig. 5) was associated with higher levels of  $f\text{CO}_2$  ( $373 \mu\text{atm}$ ),  $C_T$  ( $2128 \mu\text{mol kg}^{-1}$ ; Figs. 4a, S5a), and DSi (Fig. S6). This was also associated with higher salinity indicative of entrainment that might be related to storm events that would have occurred few days before the measurements leading to brief positive  $f\text{CO}_2$  anomaly as recently observed from glider data in the subpolar South Atlantic (Nicholson et al., 2022). As opposed to the other periods the ocean was a source of  $\text{CO}_2$  in summer 2002 (this particular year was not well reconstructed by the FFNN model; Figs. 2a and S2b). The important inter-annual variability observed in summer indicates that in this region historically referred to as HNLC (Minas



**Figure 2.** (a) Time series of sea surface  $f\text{CO}_2$  observations ( $\mu\text{atm}$ ) southwest of Kerguelen Islands in 1985–2021 (inset map shows the location of observations selected around station OISO-KERFIX at  $50^{\circ}40' \text{S}$ – $68^{\circ}25' \text{E}$ ). The color dots correspond to five periods of the year (January–February, March–April, July–August, October, and December), and triangles show the average for each month. The monthly sea surface  $f\text{CO}_2$  from the FFNN model is presented for the period 1985–2020 (grey line), and the atmospheric  $f\text{CO}_2$  is represented by the red line. In March 1985 there was no underway  $f\text{CO}_2$  observation, and the triangle corresponds to  $f\text{CO}_2$  calculated with  $A_T$  and  $C_T$  measured in the mixed layer. (b) Trends of atmospheric and oceanic  $f\text{CO}_2$  ( $\mu\text{atm}\cdot\text{yr}^{-1}$ ) in summer and winter over four different periods based on observations (January) and the FFNN model (January and August). Inset map produced with ODV (Schlitzer, 2018).

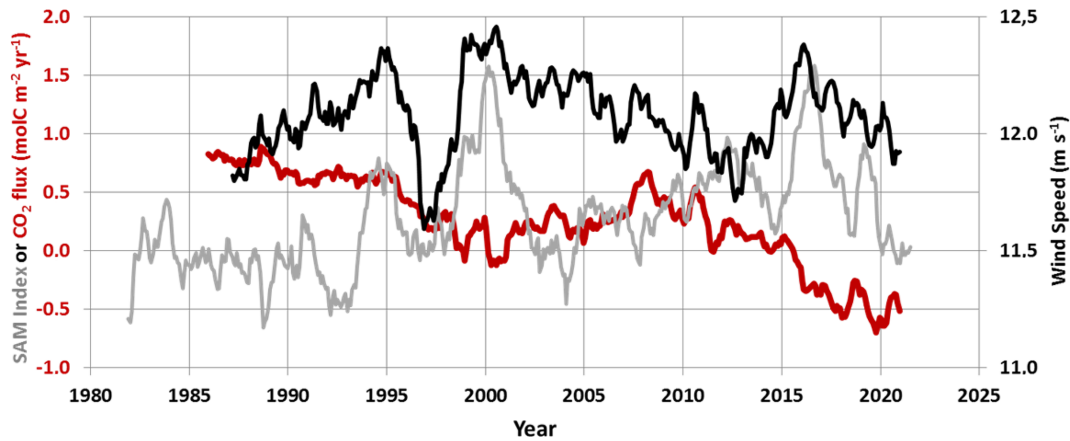
and Minas, 1992), primary production could significantly impact  $f\text{CO}_2$  levels in summer (Jabaud-Jan et al., 2004; Pasquer et al., 2015; Gregor et al., 2018), a result that needs to be taken into account when evaluating drivers of inter-annual variability (Rustogi et al., 2023) and the decadal trends of  $f\text{CO}_2$  or pH.

The Chl-*a* time series derived from MODIS suggests higher concentrations in recent years compared to 2002–2013, with Chl-*a* peaks identified in 2014, 2016, 2018, 2019, and 2021 (Figs. 5 and S7) when the oceanic  $f\text{CO}_2$  in summer was well below the atmospheric level (Fig. 2a).

The primary production lowers  $C_T$  concentrations and  $f\text{CO}_2$ , i.e., opposite to the  $C_T$  increase from anthropogenic  $\text{CO}_2$  uptake. These counteracting processes might explain the relatively stable  $f\text{CO}_2$  previously observed in the Indian POOZ in summer 2007–2019 with an annual  $f\text{CO}_2$  rate of increase of only  $+0.3 \pm 0.2 \mu\text{atm}\cdot\text{yr}^{-1}$  (Leseurre et al., 2022). This low rate is confirmed here with the recent

data obtained in 2020–2021 (Figs. 2b and S8). For the period 2010–2021, the oceanic  $f\text{CO}_2$  trend in summer derived from observations and the FFNN model is lower than  $+1 \mu\text{atm}\cdot\text{yr}^{-1}$  (Table 2), i.e., much lower than the atmospheric  $f\text{CO}_2$  rate of  $+2.4 \mu\text{atm}\cdot\text{yr}^{-1}$  and the oceanic  $f\text{CO}_2$  trend of  $+2.21 \pm 0.17 \mu\text{atm}\cdot\text{yr}^{-1}$  estimated in winter by the FFNN model (Table 2, Fig. 2b). This rate is also lower compared to the change observed in October ( $+2.9 \mu\text{atm}\cdot\text{yr}^{-1}$ ) albeit being only based on two cruises in October 2011 and 2016 (Fig. 2a). As the low  $f\text{CO}_2$  trend in recent years is detected for summer only this is likely linked to an increase in primary production, as suggested by Chl-*a* records (Fig. 5). From 1998 to 2010 the summer Chl-*a* concentrations decreased at a rate of  $-0.099 \pm 0.041 \text{ mg m}^{-3}$  per decade, whereas from 2020 to 2021 Chl *a* increased by  $+0.078 \pm 0.032 \text{ mg m}^{-3}$  per decade (Fig. 5). These trends are coherent with previous studies, e.g., the reduced net primary productivity reported in the Indian Antarctic zone over 1997–





**Figure 3.** Time series of the SAM index in the Southern Ocean (in grey), wind speed (in black,  $\text{m s}^{-1}$ ), and air–sea  $\text{CO}_2$  flux ( $\text{molC m}^{-2} \text{yr}^{-1}$ ) from the FFNN model (in red) at location  $50.5^\circ \text{S}$ – $68.5^\circ \text{E}$ . A positive (negative) flux represents a  $\text{CO}_2$  source (sink). Wind speed and SAM are presented for a 24-month running mean based on monthly values. Note the positive SAM ( $> 0.5$ ) in 1998–2002 and 2010–2019. SAM data from Marshall (2003), <http://www.nerc-bas.ac.uk/icd/gjma/sam.html> (last access: 14 August 2021). Wind speed data from ERA5 (Hersbach et al., 2020).

2007 (e.g., Arrigo et al., 2008; Takao et al., 2012) and the shift of the *Chl-*a** trend in 2010 also reported at large scale in the HNLC region of the Southern Ocean (Basterretxea et al., 2023). As a consequence, after 2010 the difference between oceanic and atmospheric  $f\text{CO}_2$  ( $\Delta f\text{CO}_2 = f\text{CO}_2^{\text{oc}} - f\text{CO}_2^{\text{atm}}$ ) decreased in summer ( $-1.4 \mu\text{atm yr}^{-1}$ ), and as it remains relatively steady during winter, the annual  $\text{CO}_2$  flux progressively varied from a source of  $+0.45 \text{ molC m}^{-2} \text{yr}^{-1}$  in 2010 to a sink of  $-0.63 \text{ molC m}^{-2} \text{yr}^{-1}$  in 2020 (Fig. 3). In addition, as the wind speed was stable during this period ( $12.0 \pm 0.9 \text{ m s}^{-1}$  on average in 2010–2020; Fig. 3), the variation of the air–sea  $\text{CO}_2$  flux was mainly controlled by  $\Delta f\text{CO}_2$  (e.g., Gu et al., 2023), and the decadal variation of primary production imprinted a significant change on the  $f\text{CO}_2$  trend and air–sea  $\text{CO}_2$  flux in this HNLC region. In the region investigated here, increasing *Chl-*a** levels co-occurred with shifts of the SAM index to a positive state (Fig. 3), a link previously suggested south of the polar front in the SO but for a short period over 1997–2004 (Lovenduski and Gruber, 2005). Modeling studies also suggest that summertime biological activity could play an important role for the variability of the  $\text{CO}_2$  sink in the SO in response to the SAM (Hauck et al., 2013).

Another process to take into account for interpreting  $f\text{CO}_2$  trends is the change in temperature in surface waters. Previous analysis suggested a progressive warming in the region investigated here (Auger et al., 2021 for summer 1993–2017). Over 1998–2019 Leseurre et al. (2022) estimated a warming of Indian POOZ surface waters of  $+0.03 \pm 0.02 \text{ }^\circ\text{C yr}^{-1}$ . Extending the time series for the period 1991–2021 (Fig. S9a), we note that the surface temperature presents sub-decadal variability and that the ocean cooled after 2018 with a trend of  $-0.47 \pm 0.16 \text{ }^\circ\text{C yr}^{-1}$  over 2018–2021 based on the monthly sea surface temperature

(SST, Fig. S9b). The trend derived from our in situ observations in summer over this period was  $-0.25 \pm 0.09 \text{ }^\circ\text{C yr}^{-1}$ .

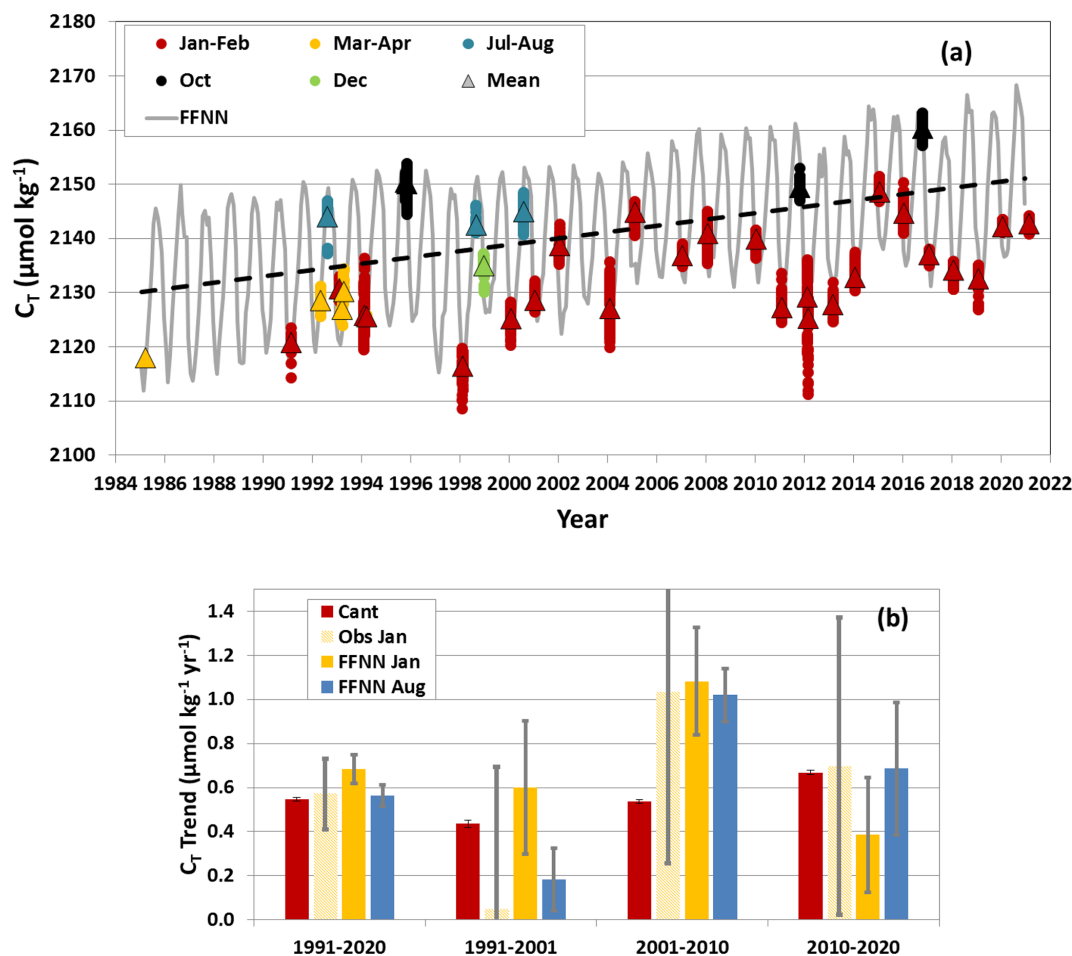
In 2019, the lower temperature and relatively high *Chl-*a** led to low  $f\text{CO}_2$  ( $380 \mu\text{atm}$ , Fig. 2a) and low  $C_T$  ( $2128 \mu\text{mol kg}^{-1}$ ) compared to 2018 ( $f\text{CO}_2 = 386 \mu\text{atm}$ ;  $C_T = 2137 \mu\text{mol kg}^{-1}$ , Fig. 4a). The decrease in observed  $f\text{CO}_2$  from summer 2018 to 2019, also reconstructed by the FFNN model (Fig. 2a), is contrary to the expected  $f\text{CO}_2$  and  $C_T$  increase due to anthropogenic uptake. In 2020, although the temperature was also lower than in 2019, the oceanic  $f\text{CO}_2$  was higher ( $392 \mu\text{atm}$ ) probably due to lower primary production as suggested by higher *DSi* (Fig. S6), as well as from  $C_T$  ( $2135 \mu\text{mol kg}^{-1}$ , Fig. 4a) and *Chl-*a** records (Fig. 5). In January 2021 the temperature was close to that in January 2020, and both  $f\text{CO}_2$  and  $C_T$  were slightly higher ( $395 \mu\text{atm}$ ,  $2139 \mu\text{mol kg}^{-1}$ ).  $A_T$  concentrations were stable between 2018 and 2021 ( $2278.9 \pm 1.8 \mu\text{mol kg}^{-1}$ , Fig. S5), indicating no effect of  $A_T$  on the observed  $f\text{CO}_2$  change in this region as opposed to the areas north of the polar front in the Indian Ocean where  $A_T$  variations are often linked to coccolithophore blooms (Balch et al., 2016; Smith et al., 2017).

The inter-annual and pluri-annual variability observed over 1991–2021 highlights the competitive processes that drive  $C_T$ ,  $f\text{CO}_2$ , or pH temporal variations. In order to separate natural and anthropogenic contributions, the anthropogenic  $\text{CO}_2$  signal is estimated in the following section.

## 3.2 Anthropogenic $\text{CO}_2$

### 3.2.1 Anthropogenic $\text{CO}_2$ in the water column

To calculate anthropogenic  $\text{CO}_2$  concentrations ( $C_{\text{ant}}$ ), we used the TrOCA method developed by Touratier et al. (2007) and previously applied in the southern Indian Ocean (Mahieu



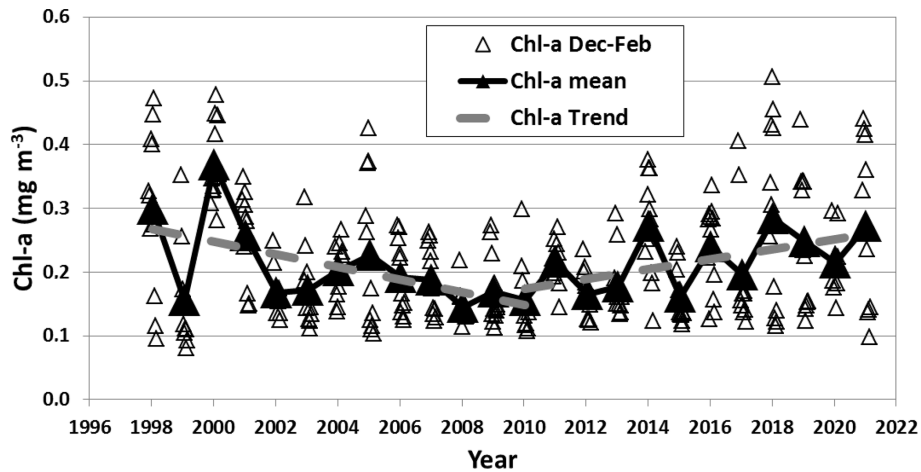
**Figure 4.** (a) Time series of surface  $C_T$  ( $\mu\text{mol kg}^{-1}$ ) around station OISO-KERFIX at  $50^{\circ}40' \text{ S}$ – $68^{\circ}25' \text{ E}$  calculated from  $f\text{CO}_2$  data (Fig. 2) using the  $A_T$ – $S$  relation (see Sect. 2.2.5). The color dots correspond to five periods of the year (January–February, March–April, July–August, October, and December), and triangles show the average for each month. The monthly sea surface  $C_T$  from the FFNN model is presented for the period 1985–2020 (grey line). The annual  $C_T$  trend of  $+0.58 \pm 0.05 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$  (dashed line) is derived from the FFNN monthly data. In March 1985 the triangle corresponds to the observed  $C_T$  in the mixed layer. (b) Trends of sea surface  $C_T$  ( $\mu\text{mol kg}^{-1} \text{ yr}^{-1}$ ) in summer and winter over four different periods based on observations (for January) and the FFNN model (for January and August). The trend for  $C_{\text{ant}}$  ( $\mu\text{mol kg}^{-1} \text{ yr}^{-1}$ ) is also shown (red bars) based on estimates in the winter water.

et al., 2020; Leseurre et al., 2022). Such an indirect method is not suitable for evaluating  $C_{\text{ant}}$  concentrations in surface waters due to biological activity and gas exchange, and we restrict the  $C_{\text{ant}}$  calculations below the productive layer around 150 m. In the region south of the polar front, a well-defined subsurface temperature minimum is observed each year characterizing the winter water (WW) at a depth range of 150–250 m (Fig. 6a).

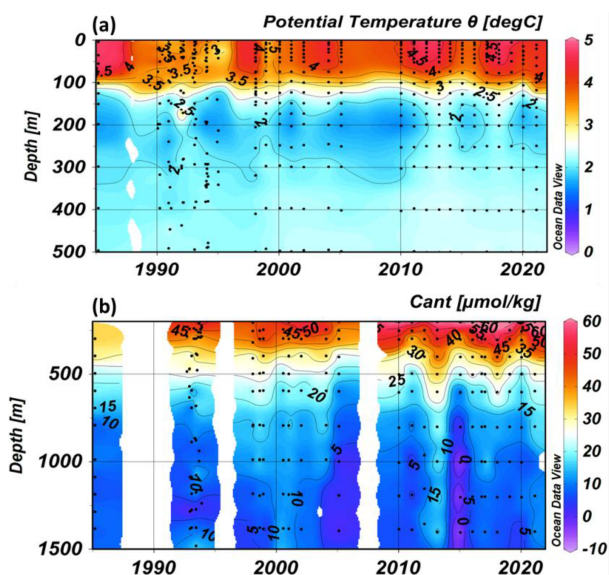
The  $C_T$  and  $C_{\text{ant}}$  concentrations increased over time in the water column, a signal that is most pronounced in the top layers (200–400 m, Fig. 6b). In the deep layer, the presence of the Indo-Pacific Deep Water (IPDW) around 600–800 m is identified by a maximum of  $C_T$  ( $C_T > 2250 \mu\text{mol kg}^{-1}$ ) and a minimum of  $\text{O}_2$  ( $\text{O}_2$  close to or  $< 180 \mu\text{mol kg}^{-1}$ , Fig. S10) (Talley, 2013; Chen et al., 2022). In the IPDW layer restricted to the neutral density (ND) range 27.75–

$27.85 \text{ kg m}^{-3}$ , there is no significant change in  $C_T$  over time (Fig. S10). In that layer the  $C_{\text{ant}}$  concentrations in 1985 ( $17.3 \mu\text{mol kg}^{-1}$ ) were almost identical to those evaluated in 2021 ( $21.2 \mu\text{mol kg}^{-1}$ ), considering the uncertainty in the  $C_{\text{ant}}$  calculations ( $\pm 6.5 \mu\text{mol kg}^{-1}$ ; Touratier et al., 2007). Below 800 m, the  $C_{\text{ant}}$  concentrations were small but not null (Fig. 6b). The average  $C_{\text{ant}}$  concentration below 800 m for all years and seasons was  $8.0 \pm 5.3 \mu\text{mol kg}^{-1}$  ( $n = 123$ ) with a very small change detected over time ( $C_{\text{ant}} = 7.7 \pm 1.3 \mu\text{mol kg}^{-1}$  in 1985 and  $C_{\text{ant}} = 10.4 \pm 0.6 \mu\text{mol kg}^{-1}$  in 2021). As discussed above (Sect. 2.2.3) the  $C_T$  and  $A_T$  concentrations in the bottom layer ( $> 1450 \text{ m}$ ) were stable over 1985–2021 (Table S2, Fig. S1).





**Figure 5.** Time series (1998–2021) of sea surface Chl *a* ( $\text{mg m}^{-3}$ ) in summer (December–February) from weekly satellite data (SeaWiFS and MODIS, open triangles) and associated mean (black triangles). The trends in 1998–2010 and 2010–2021 of respectively  $-0.0099 \pm 0.0041$  and  $+0.0078 \pm 0.0032 \text{ mg m}^{-3} \text{ yr}^{-1}$  (dashed grey) indicate a decrease or increase of the primary production. The full Chl-*a* record is shown in Fig. S7.



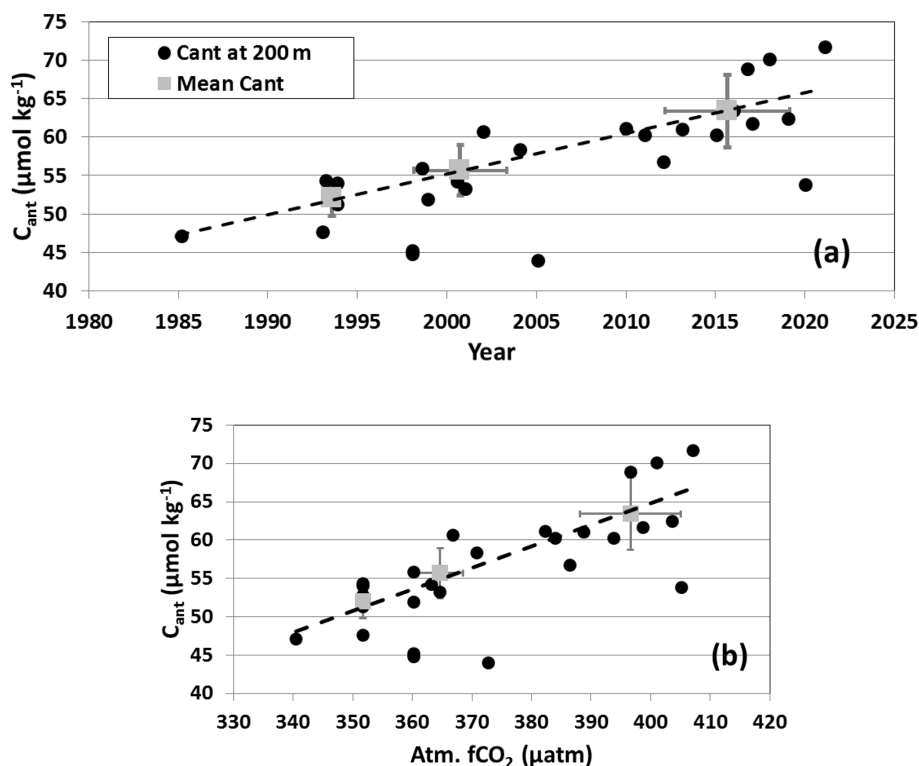
**Figure 6.** Hovmöller section (depth–time) of (a) potential temperature ( $^{\circ}\text{C}$ ) and (b) anthropogenic  $\text{CO}_2$  ( $C_{\text{ant}}$ ,  $\mu\text{mol kg}^{-1}$ ) over 1985–2021 at station OISO-KERFIX ( $50^{\circ}40' \text{ S}$ – $68^{\circ}25' \text{ E}$ ). The section for temperature is presented in the layer 0–500 m and for summer to highlight the temperature minimum around 200 m (winter water, WW). The section for  $C_{\text{ant}}$  is limited below 200 m. Section produced with ODV (Schlitzer, 2018).

### 3.2.2 Anthropogenic $\text{CO}_2$ trend in the winter water

To separate the natural and anthropogenic signals in surface waters for the driver analysis, we assume that  $C_{\text{ant}}$  in the WW is representative of  $C_{\text{ant}}$  in the mixed layer (ML). This is confirmed with few stations occupied during winter showing that  $C_{\text{ant}}$  concentrations in the WW in summer are almost equal

to  $C_{\text{ant}}$  in the ML during the preceding winter (Fig. S11). The evolution of  $C_{\text{ant}}$  in the WW from 1985 to 2021 is presented in Fig. 7a for all seasons. In 1985 the  $C_{\text{ant}}$  concentration in the WW was  $47.1 \mu\text{mol kg}^{-1}$ , and  $C_{\text{ant}}$  reached a maximum of  $71.7 \mu\text{mol kg}^{-1}$  in 2021. The data selected at 200 m present some inter-annual variability such as the relatively low  $C_{\text{ant}}$  in 1998, 2005, and 2020 probably related to natural variability. In 1998 and in 2020 the  $\text{O}_2$  concentrations were slightly lower in the WW ( $< 300 \mu\text{mol kg}^{-1}$ ), explaining the lower  $C_{\text{ant}}$  concentration ( $44.8 \mu\text{mol kg}^{-1}$  in 1998 and  $53.8 \mu\text{mol kg}^{-1}$  in 2020), but no anomaly was observed for  $C_{\text{T}}$ . This suggests that the biological contribution may have been overestimated (lower  $\text{O}_2$  is interpreted by the TrOCA method as more organic matter remineralization which should be associated with higher  $C_{\text{T}}$ ). This could be instead related to a change in mixing or circulation. In 2005 anomalies of  $C_{\text{T}}$ ,  $A_{\text{T}}$ , and  $\text{O}_2$  concur to explain the lower  $C_{\text{ant}}$  ( $43.9 \mu\text{mol kg}^{-1}$ ).

From 1985 to 2021, we estimated a  $C_{\text{ant}}$  trend in WW of  $+0.49 \pm 0.09 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$ . When the  $C_{\text{ant}}$  anomalies in 1998, 2005, and 2020 were discarded, this  $C_{\text{ant}}$  trend was  $+0.53 \pm 0.01 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$  (Fig. 7a). As expected, the  $C_{\text{ant}}$  concentrations in the ocean are positively related to atmospheric  $\text{CO}_2$  (slope  $+0.26 \pm 0.04 \mu\text{mol kg}^{-1} \mu\text{atm}^{-1}$ ; Fig. 7b). Interestingly, the slope observed south of the PF in the Indian Ocean is close to that observed in the Antarctic Intermediate Water (AAIW) in the South Atlantic ( $+0.23 \pm 0.05 \mu\text{mol kg}^{-1} \mu\text{atm}^{-1}$ ; Fontela et al., 2021). Gruber et al. (2019a, b) evaluated  $C_{\text{ant}}$  changes between 1994 and 2007 in the global ocean. In the southern Indian sector, they estimated a mean  $C_{\text{ant}}$  accumulation at the surface of  $+6.0 \pm 1.1 \mu\text{mol kg}^{-1}$  in the band  $50$ – $55^{\circ} \text{ S}$  south of the PF. At our station location ( $50$ – $52^{\circ} \text{ S}$ ,  $68^{\circ} \text{ E}$ ) in the layer 0–250 m, the  $C_{\text{ant}}$  accumulated from 1994 to



**Figure 7.** (a) Time series of anthropogenic CO<sub>2</sub> ( $C_{\text{ant}}$   $\mu\text{mol kg}^{-1}$ ) estimated in the winter water layer (WW around 200 m; see Fig. 6) from 1985 to 2021 at station OISO-KERFIX (50°40' S–68° 25' E). Black dots are the individual data in the WW and the grey squares the average for the 1990s, 2000s, and 2010s (anomalies in 1998, 2005, and 2020 discarded). The  $C_{\text{ant}}$  trend of  $+0.53 \pm 0.01 \mu\text{mol kg}^{-1} \text{yr}^{-1}$  is represented (dashed line). (b) Same data for  $C_{\text{ant}}$  versus atmospheric  $f\text{CO}_2$  (the slope is  $+0.263 \pm 0.042 \mu\text{mol kg}^{-1} \mu\text{atm}^{-1}$ ).

2007 was  $+5.7 \pm 1.5 \mu\text{mol kg}^{-1}$ . In 13 years, this corresponds to a trend of  $+0.44 \pm 0.11 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ . Gruber et al. (2019a, b) did not use the data presented here, allowing for an independent comparison to the present study. Estimates of  $C_{\text{ant}}$  accumulation by Gruber et al. (2019a, b) are in agreement with ours for the period 1994–2007 ( $+0.49 \pm 0.01 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ ) but lower than reported here in recent years ( $+0.61 \pm 0.01 \mu\text{mol kg}^{-1} \text{yr}^{-1}$  over 2008–2021). Indeed our estimates over 3 decades indicate an increase in the uptake of anthropogenic CO<sub>2</sub> with time (Fig. 4b).

### 3.2.3 Anthropogenic and surface $C_T$ seasonal trends

The  $C_{\text{ant}}$  trend in the WW over 1985–2021 ( $+0.53 \pm 0.01 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ ) is slightly lower than the annual surface  $C_T$  trend derived from the FFNN model for 1985–2020 ( $+0.58 \pm 0.05 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ ; Fig. 4a, Table 2) suggesting that anthropogenic CO<sub>2</sub> uptake explains 86 % of the  $C_T$  increase in surface waters. Over 1991–2020 the surface  $C_T$  trend appears slightly higher in January than in August (Fig. 4b, Table 2). This suggests that in addition to the increase of  $C_T$  due to anthropogenic CO<sub>2</sub>, other processes such as the variability of the biological activity, vertical mixing, or upwelling contributed to the observed trend. Indeed, as for  $f\text{CO}_2$  (Fig. 2b), the  $C_T$  growth rate also depends on seasons

and decades (Fig. 4b). Over 1991–2001 the  $C_T$  trend from the observations ( $+0.05 \pm 0.64 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ ; Table 2) is highly uncertain due to few data and the large variability (Fig. 4a, b). The FFNN model showed that the  $C_T$  trend in summer was faster than the trend in  $C_{\text{ant}}$  (Fig. 4b), suggesting that natural processes would have increased  $C_T$ . This could be explained by an increase in vertical mixing due to the increase in wind speed (Fig. 3). On the contrary, the winter  $C_T$  trend was lower than the  $C_{\text{ant}}$  trend estimated in subsurface waters (Fig. 4b).

Over 2001–2010 the  $C_T$  trends were much faster than over the previous decade, and they were the same for both seasons (Fig. 4b, Table 2). For this decade the summer  $C_T$  trends from the observations and the FFNN model are coherent. They were also twice the  $C_{\text{ant}}$  rate in the WW, which could be explained by enhanced upwelling of  $C_T$ -rich deep waters during this period after the SAM reached a high positive index (Fig. 3; Lenton and Matear, 2007; Le Quéré et al., 2007; Hauck et al., 2013). However, over this period we did not detect any clear change at depth for ocean properties (except for  $C_T$  and  $C_{\text{ant}}$ ) that would support this assumption (enhanced upwelling). The rapid  $C_T$  (and  $f\text{CO}_2$ ) trend for this decade is probably due to processes occurring at the surface (e.g., biological activity, as discussed later) rather than

changes in the water column (vertical mixing or upwelling). Over the last decade  $C_T$  trends were lower than over the previous one (Fig. 4b). For summer, this is identified from both observations and the FFNN model. In winter the  $C_T$  trend (from FFNN) is close to  $C_{ant}$ , indicative of the anthropogenic  $CO_2$  accumulation. The low  $C_T$  trend at the surface in summer, about half the  $C_{ant}$  trend, is likely due to the increase of primary production after 2010 as described above (Fig. 5). Thus, it appears that the impact of biological activity and its variability in summer could counteract that of anthropogenic  $CO_2$  and explain the low temporal change of the carbonate system at the surface in recent years.

Given the differences of the  $fCO_2$  and  $C_T$  trends in summer and winter (Figs. 2b and 4b, Table 2), we explored the temporal variations of the seasonality. For each year we estimated the differences between August and January (Fig. 8a). The seasonal amplitude for  $C_T$  was on average  $26.1 \pm 3.4 \mu\text{mol kg}^{-1}$  and for  $fCO_2$   $15.1 \pm 5.6 \mu\text{atm}$ . Some large inter-annual variations appear related to the variability of Chl *a* in summer (Fig. 8a). Interestingly, the  $fCO_2$  seasonal amplitude reached a minimum around 2008–2010 and then increased over 2010–2020. This signal also appears correlated with the evolution of surface Chl *a* in summer (Fig. 8). This supports the conclusion that low phytoplanktonic biomass between 2008 and 2010 reduced the seasonal amplitude of  $fCO_2$ .

The inter-annual variability of the seasonality is clearly identified when comparing  $C_T$  with  $C_T$  calculated due only to  $C_{ant}$  accumulation (Fig. S12). This supports the conclusion that in addition to the  $C_{ant}$  accumulation, the variations of phytoplanktonic biomass imprinted inter-annual variability on  $C_T$  and  $fCO_2$  in summer. This holds for the seasonal amplitude as the results for winter follows the  $C_{ant}$  trend (Figs. 4b, S12a). The same is true for pH for which reduced seasonal amplitude was found when the production was low (not shown). However, over 36 years (1985–2020) we did not identify a long-term trend of the seasonal amplitude for  $C_T$  or for  $fCO_2$  as suggested by other studies (Landschützer et al., 2018; Rodgers et al., 2023; Shadwick et al., 2023). Our results highlight a variability over 5–10 years (Fig. 8a) and suggest a potential change in seasonality and annual  $CO_2$  sink if primary production changes in the future (e.g., Bopp et al., 2013; Leung et al., 2015; Fu et al., 2016; Kwiatkowski et al., 2020; Krumhardt et al., 2022; Seifert et al., 2023).

### 3.3 Anthropogenic $CO_2$ drives acidification in surface waters and in the water column

#### 3.3.1 Surface pH trend

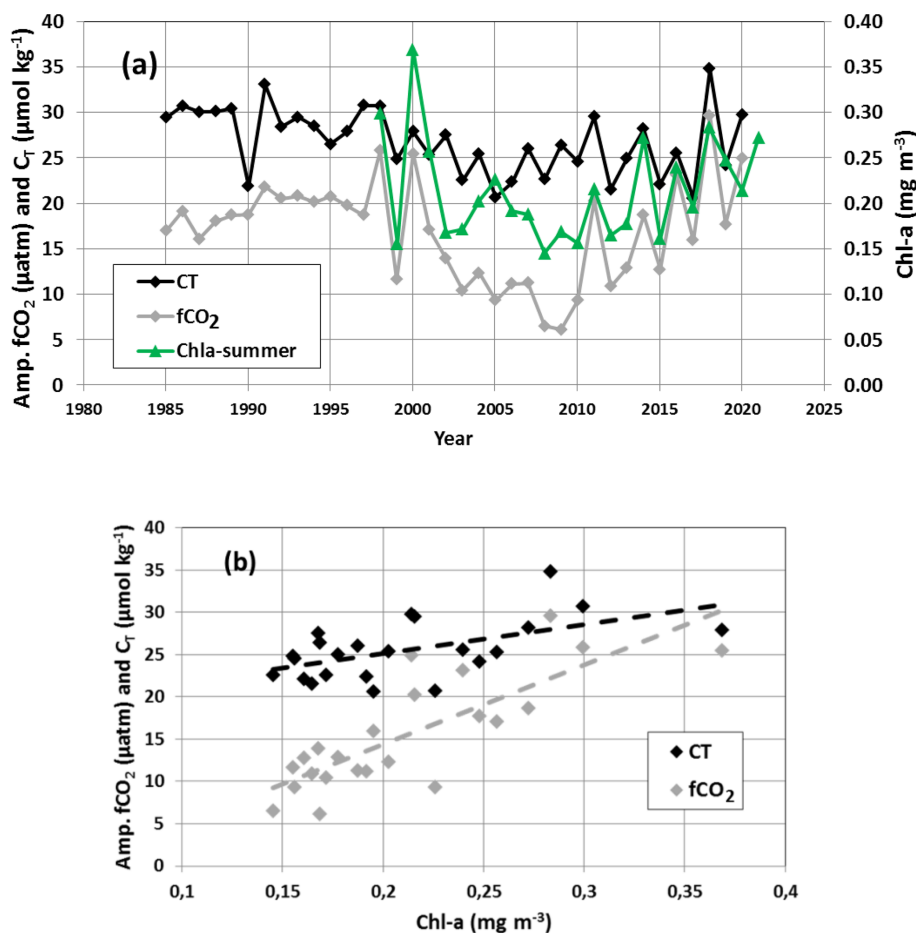
To explore the temporal change of pH in surface waters, we used the  $fCO_2$  observations and the monthly results from the FFNN model. For both datasets pH was calculated from  $fCO_2$  and  $A_T$  reconstructed as described in Sect. 2.2.5. Figure 9a presents the time series of pH at the surface (the same

time series for  $[H^+]$  concentrations is shown in Fig. S13). For the full period, 1985–2020, the annual pH trend derived from the FFNN model is  $-0.0165 \pm 0.0004$  per decade (Table 2), exactly the same as derived at large scale in the Southern Ocean (south of  $44^\circ\text{S}$ ) for the period 1993–2018 (Iida et al., 2021, Table 1), but when restricted to this period, 1993–2018, the trend from the FFNN model appears slightly faster ( $-0.0182 \pm 0.0006$  per decade). This is less than the pH trend derived from  $pCO_2$  data in the SO subpolar seasonally stratified biome around  $40\text{--}50^\circ\text{S}$  (SO-SPSS) for 1981–2011 ( $-0.020 \pm 0.002$  per decade; Table 1; Lauvset et al., 2015) and close to the pH trend based on OceanSODA-ETH reconstructed fields in the SO-SPSS for the period 1982–2021 ( $-0.0189 \pm 0.0010$  per decade; Ma et al., 2023). However, as for  $fCO_2$  and  $C_T$ , we estimated different pH trends in summer and winter, depending on the periods (Fig. 9b, Table 2).

The winter pH decrease estimated over the last 2 decades was twice as fast as estimated during the previous one, mirroring the winter  $fCO_2$  trends (Table 2). In summer, the pH trend presents a large variability at decadal scale as it was 3 times faster over 2001–2010 than during the previous and following decades (Fig. 9b, Table 2). Although the trends based on the observations are less robust because the cruises were not conducted each year, the reduced pH trend in summer after 2010 is confirmed from in situ data (Fig. 9b, Table 2).

Our results show that the pH trend varied significantly from decade to decade and that part of the variations could be explained by the evolution of phytoplanktonic biomass, but overall the decrease of pH since 1985 was mainly driven by the accumulation of anthropogenic  $CO_2$ . This is revealed in the winter water when comparing pH and pre-industrial pH (Fig. 10a). Here, the pre-industrial pH (pH-PI) was calculated after subtracting  $C_{ant}$  values from the observed  $C_T$  concentrations for each sample in the WW layer. Interestingly, the pH trend in the WW of  $-0.0161 \pm 0.0033$  per decade (here deduced from the station  $A_T$  and  $C_T$  data over 1985–2021) is very close to the annual trend at the surface deduced from the FFNN model over 1985–2020 ( $-0.0165 \pm 0.0004$  per decade). This trend is slightly faster than the pH trends of  $-0.0134 \pm 0.001$  per decade recently estimated in subsurface waters (100–210 m) of the Southern Ocean south of the PF and derived for years 1994–2017 from historical data and BGC-Argo floats (Mazloff et al., 2023). For the same period, 1994–2017, at the OISO-KERFIX station we estimated a pH trend in the WW of  $-0.0168 \pm 0.0043$  and of  $-0.0186 \pm 0.0006$  per decade in surface waters from the FFNN model.

As for other properties ( $A_T$ ,  $O_2$ , temperature, salinity, and nutrients), the pre-industrial pH (pH-PI) does not change over time in the WW (mean pH-PI =  $8.173 \pm 0.020$ ,  $n = 45$ ; Fig. 10a). The pH-PI in the WW is in the range of the pre-industrial surface pH value in the Southern Ocean (8.2 for year 1750 and 8.18 for year 1850) derived from Earth system models (Jiang et al., 2023, their Table S9). In the WW



**Figure 8.** (a) Time series of the seasonal amplitude (August minus January) for surface  $C_T$  (black;  $\mu\text{mol kg}^{-1}$ ) and  $f\text{CO}_2$  (grey;  $\mu\text{atm}$ ) from the FFNN model at station OISO-KERFIX ( $50^\circ 40' \text{S}$ – $68^\circ 25' \text{E}$ ). Also shown are the mean surface Chl  $a$  values (green;  $\text{mg m}^{-3}$ ) in summer from 1998 to 2021. (b) Seasonal amplitude of  $f\text{CO}_2$  and  $C_T$  versus summer Chl  $a$  over 1998–2020. The dashed lines indicate that the seasonal amplitude (August–January) increases when Chl  $a$  is higher.

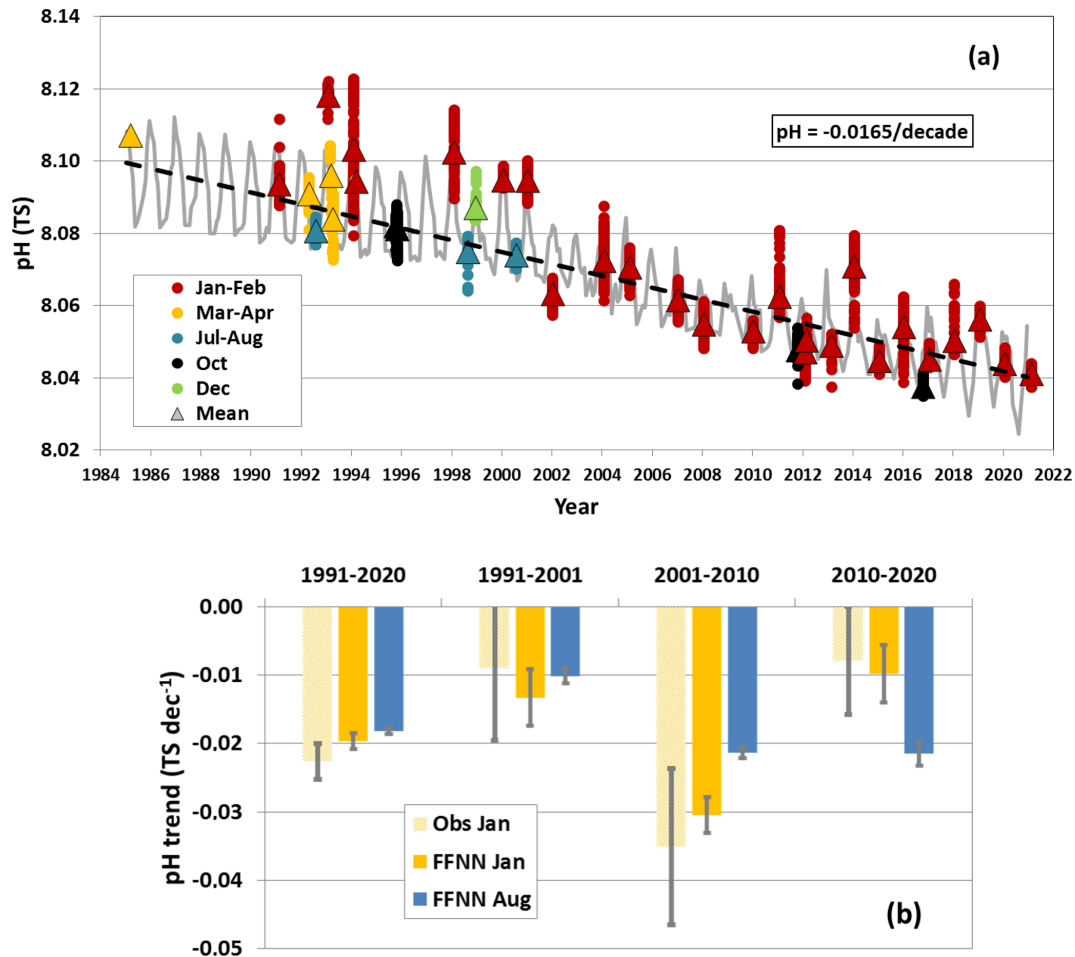
at our location the modern pH (1985–2021) was on average  $-0.147 \pm 0.021$  lower than pre-industrial pH. In 1985 pH in the WW was  $-0.119$  lower than pH-PI, and in 2021 it was  $-0.184$  lower than pH-PI (Fig. 10a). The progressive decrease of pH was clearly linked to  $C_{\text{ant}}$  concentrations in the WW layer and the pH decrease identified below that layer in the water column (Fig. 10b).

### 3.3.2 Temporal change in the water column

From 1985 to 2021, signals of decreasing pH and increasing  $C_T$  in surface waters are propagated in the water column down to about 500 m. As mentioned above the data in 1985 (first occupation of the station) reveal significant  $C_{\text{ant}}$  levels across the water column (Fig. 6b). Therefore the pH down to the bottom was already lower in 1985 than at pre-industrial times (Fig. 10b). However, the largest  $C_{\text{ant}}$  increases were found in the top layers, and changes in pH from 1985 to 2021 were small below 500 m (Figs. 10b, S14). While observations for all years fall on a common linear relationship

between  $C_{\text{ant}}$  and  $\text{pH}_{\text{ant}}$  for depths greater than 500 m, the change in pH for a given level of  $C_{\text{ant}}$  increases with time for layers shallower than 500 m (Fig. 11).

The increase in  $C_{\text{ant}}$  concentrations over time (Fig. 6b) also leads to a decrease of carbonate ion concentrations [ $\text{CO}_3^{2-}$ ] and of  $\Omega\text{Ar}$  and  $\Omega\text{Ca}$  (Figs. S14, S15). These decreases are well identified since the pre-industrial era in the whole water column, but in the last 36 years observations do not show any appreciable changes below 500 m (Fig. 11). The aragonite saturation horizon ( $\Omega\text{Ar}=1$ ) was found around 600 m in 1985 and around 400 m in recent years (2015–2021; Figs. S14, S15). Moreover, during the period covered by observations (1985–2021), we did not detect abrupt change of the aragonite saturation horizon from one year to the next (nor between winter and summer; Fig. S16). This contrasts with previous regional studies in the SO and most notably with results from the layers close to the deep minimum of carbonate ion concentrations (Hauri et al., 2015; Negrete-García et al., 2019). At our station the [ $\text{CO}_3^{2-}$ ] minimum lies



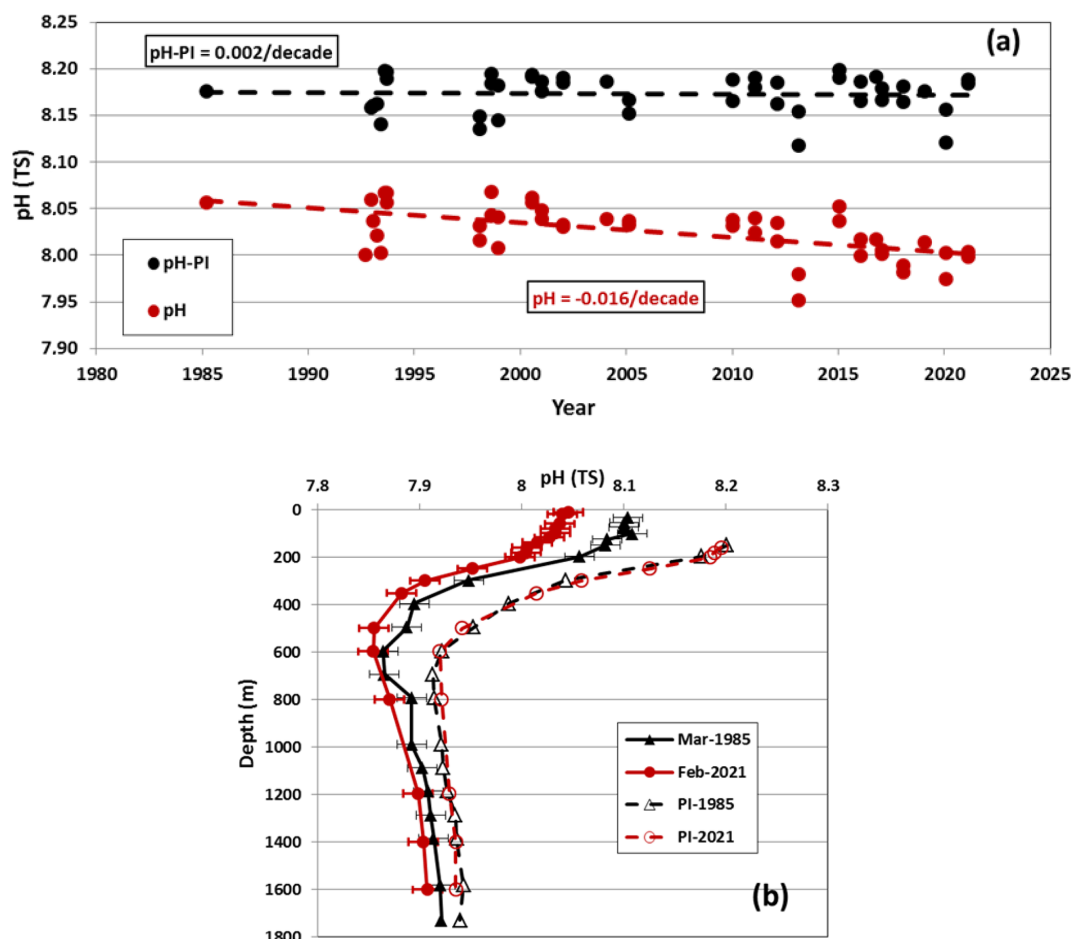
**Figure 9.** (a) Time series of surface pH (total scale, TS) around station OISO-KERFIX(50°40′ S–68°25′ E) calculated from  $f\text{CO}_2$  data (Fig. 2) using the  $A_T$ – $S$  relation (see Sect. 2.2.5). The color dots correspond to five periods of the year (January–February, March–April, July–August, October, and December), and triangles show the average for each month. The monthly sea surface pH from the FFNN model is presented for the period 1985–2020 (grey line). The annual pH trend in 1985–2020 of  $-0.0165 \pm 0.0004$  per decade (dashed line) is derived from the FFNN monthly data (the same figure for  $[\text{H}^+]$  concentrations is presented in Fig. S13). (b) Trends of pH (TS per decade) in summer and winter over four different periods based on observations (January) and the FFNN model (January and August).

around 500–600 m (Figs. S14, S15) and, along with the superimposed  $C_{\text{ant}}$  accumulation, explains the upward shift of the aragonite and calcite saturation horizon between the pre-industrial and modern periods (Fig. S15). At pre-industrial time undersaturation with regard to aragonite ( $\Omega_{\text{Ar}} < 1$ ) was found at the bottom only (1600 m), whereas between 1985 and 2021 it was found in the water column below 600 or 400 m (Fig. S15). The subsurface pre-industrial  $\Omega_{\text{Ar}}$  value was around 1.9–2 (Fig. S15) and in the range of  $\Omega_{\text{Ar}}$  value in the Southern Ocean at pre-industrial time from ESMs (Jiang et al., 2023, their Fig. 4).

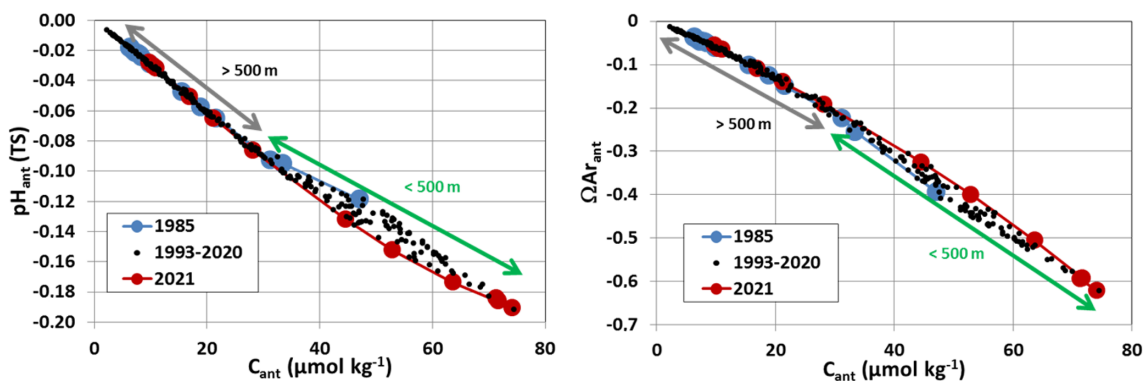
The aragonite undersaturation already occurred in 1985 at 600–700 m, a layer corresponding to the  $[\text{CO}_3^{2-}]$  minimum (Fig. S15), and a small increase of  $C_T$  just above this layer (via  $C_{\text{ant}}$  accumulation) would rapidly shift the aragonite saturation horizon above 600 m. This might have already oc-

curred and could explain that  $\Omega_{\text{Ar}}$  value was 1.02 at 350 m in 2021 (Fig. S15). These results suggest that for pelagic calcifiers living in subsurface waters (150 m or deeper) such as pteropods and foraminifera (e.g., Hunt et al., 2008; Meilland et al., 2018), the impact of acidification might occur sooner than at the surface.

For the interpretation of the trend analysis based on observations, only data below 150 m could be used as  $C_{\text{ant}}$  was not evaluated in the surface layer. At 200 m, based on  $A_T$  and  $C_T$  data, we estimated a decrease in pH from 1985 to 2021 by  $-0.059$  (Fig. 10b), corresponding to an increase by  $+1.1 \text{ nmol kg}^{-1}$  in  $[\text{H}^+]$  (Fig. S13) and a decrease by  $-0.16$  in  $\Omega_{\text{Ar}}$  (Fig. S15). Over 36 years, this represents about 30 % of the total change since the pre-industrial era for pH ( $-0.184$ ),  $[\text{H}^+]$  ( $+3.5 \text{ nmol kg}^{-1}$ ), and  $\Omega_{\text{Ar}}$  ( $-0.6$ ). This is mainly linked to the  $C_{\text{ant}}$  change that



**Figure 10.** (a) Time series of pH (red dots) and pre-industrial pH (pH-PI; black dots) estimated in the winter water layer (WW around 200 m; see Fig. 6) over 1985–2021 at station OISO-KERFIX ( $50^{\circ}40' \text{ S}$ – $68^{\circ}25' \text{ E}$ ). pH-PI for each sample was calculated after subtracting  $C_{\text{ant}}$  to  $C_{\text{T}}$ . The pH trend from the present day is  $-0.0161 \pm 0.0033$  per decade (dashed red line). No trend is observed for pH-PI (dashed black). The mean pH-PI in the WW is  $8.173 \pm 0.020$  ( $n = 45$ ). (b) Profiles of pH and pH-PI evaluated from March 1985 (black symbols) and February 2021 data (red symbols). The profiles for pH-PI are shown below 150 m only as  $C_{\text{ant}}$  estimates are not available in the surface layer. Note that the pH-PI profiles are the same either using either the 1985 or 2021 data.



**Figure 11.** Anthropogenic pH ( $\text{pH}_{\text{ant}}$ ) and anthropogenic  $\Omega\text{Ar}$  ( $\Omega\text{Ar}_{\text{ant}}$ ) versus anthropogenic  $\text{CO}_2$  concentrations ( $C_{\text{ant}}$ ,  $\mu\text{mol kg}^{-1}$ ) at station OISO-KERFIX ( $50^{\circ}40' \text{ S}$ – $68^{\circ} 25' \text{ E}$ ). The data are selected in the layer 150–1600 m for the periods 1985 (blue), 1993–2020 (black), and 2021 (red). The green arrow identifies the data in the layer 150–500 m (for  $C_{\text{ant}} > 30 \mu\text{mol kg}^{-1}$ ). Below 500 m (brown arrow) no change of  $C_{\text{ant}}$  was observed from 1985 to 2021 and thus for  $\text{pH}_{\text{ant}}$  and  $\Omega\text{Ar}_{\text{ant}}$ .



also represents over 36 years 30 % of the total accumulation ( $+24.6 \mu\text{mol kg}^{-1}$  from 1985 to 2021 for a total concentration of  $+71.7 \mu\text{mol kg}^{-1}$  at 200 m in 2021; Fig. 7). We conclude that the accumulation of anthropogenic  $\text{CO}_2$  drives the change of the carbonate system in subsurface waters and probably also in surface waters.

In order to quantify the propagation of surface trends to depth, the temporal variations of carbonate system properties at the surface for both summer and winter derived from the FFNN model are compared to the changes observed across the water column (Fig. 12). The comparison shows that the seasonal amplitude of surface waters properties was of a similar magnitude to the observed changes in the mixed layer between 1985 and 2021. For example, the  $C_T$  and  $\Omega\text{Ar}$  seasonal amplitude, respectively around  $20 \mu\text{mol kg}^{-1}$  and 0.2, correspond to the  $C_T$  increase and  $\Omega\text{Ar}$  decrease from 1985 to 2021. The comparisons also highlight that in summer the FFNN results were close to observations in the mixed layer (e.g.,  $C_T$  was  $2120 \mu\text{mol kg}^{-1}$  in 1985 and  $2140 \mu\text{mol kg}^{-1}$  in 2021). In winter, at the surface,  $C_T$  was higher and pH,  $[\text{CO}_3^{2-}]$ , and  $\Omega\text{Ar}$  were lower (from the FFNN model; blue line in Fig. 12). The winter surface values in 1985 and 2020/2021 are in good agreement with observations at depth in the winter water (150–200 m). As an example, in 1985 surface  $C_T$  in winter was  $2145.5 \mu\text{mol kg}^{-1}$ , which corresponds to the concentration measured at 150 m during summer (purple line in Fig. 12). In 2020, the winter  $C_T$  at the surface ( $2168.3 \mu\text{mol kg}^{-1}$ ) is equal to  $C_T$  concentrations observed at 150–180 m in January 2020 or in 2021. For  $\Omega\text{Ar}$ , the surface value derived from the FFNN model in winter 1985 (1.6) was equal to the  $\Omega\text{Ar}$  observed at 125 m in March 1985. In 2020, the surface winter estimate of  $\Omega\text{Ar}$  (1.42) was equal to  $\Omega\text{Ar}$  observed at 100–150 m in January 2020 or 2021. The same correspondences between winter surface and WW data were identified for pH and  $[\text{CO}_3^{2-}]$  (Fig. 12). This supports the use of winter and summer surface data from the FFNN model to investigate the seasonal  $\Omega\text{Ar}$  trends and their projection in the future.

The surface water  $\Omega\text{Ar}$  ( $\Omega\text{Ca}$ ) trend from the FFNN model in summer of  $-0.0059 \text{ yr}^{-1}$  ( $-0.0094 \text{ yr}^{-1}$ ) was stronger than the winter of  $-0.0050 \text{ yr}^{-1}$  ( $-0.0079 \text{ yr}^{-1}$ ) and also higher than the trend derived from observations in the WW ( $-0.0043 \text{ yr}^{-1}$  for  $\Omega\text{Ar}$  and  $-0.0069 \text{ yr}^{-1}$  for  $\Omega\text{Ca}$ ). Our results indicate that the change of carbonate properties in the years 1985–2021 were mainly driven by  $C_{\text{ant}}$  accumulation in surface waters and across the water column. However, a potential increase in primary productivity after 2010 mitigated the effects of increasing  $C_{\text{ant}}$  accumulation in response to increasing atmospheric  $\text{CO}_2$  leading to relatively stable summer  $C_T$  and  $f\text{CO}_2$  and to a stronger  $\text{CO}_2$  sink (Fig. 3). Consequently, when restricted to the period 2010–2020, the trend of  $\Omega\text{Ar}$  in surface waters in summer was much smaller,  $-0.024 \pm 0.027$  per decade than during the preceding period. This was much smaller than derived from all the data over 1985–2021 ( $-0.048$  per decade) or estimated from re-

constructed fields in the SO-SPSS over 1982–2021 ( $-0.0616$  per decade; Ma et al., 2023). It underscores the uncertainty in extrapolating time series to the future depending on the selection of data and periods.

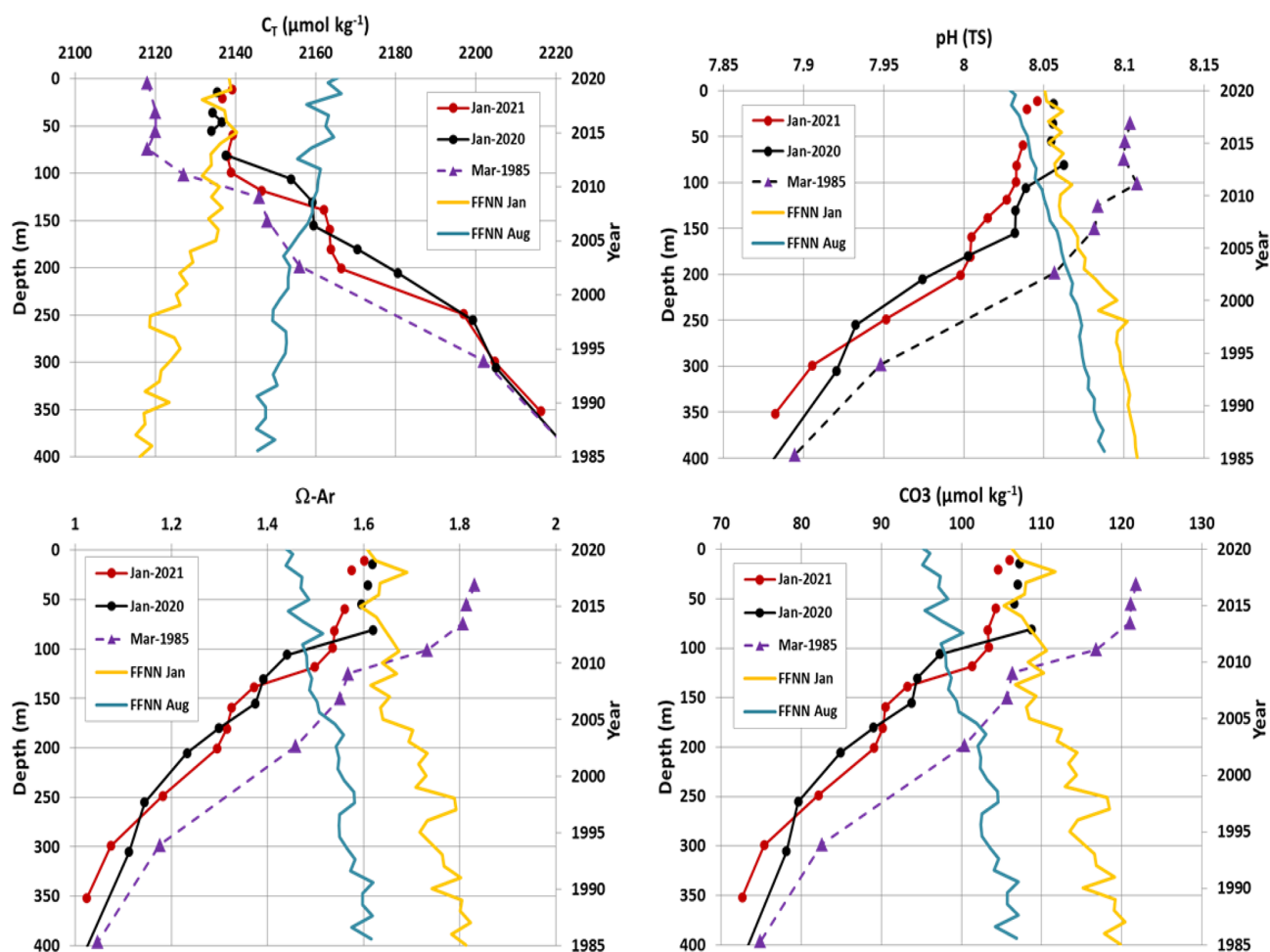
### 3.4 Long-term change in surface water: from the 1960s to the future

The data described above allowed evaluating the temporal variations of the properties of the carbonate system and  $C_{\text{ant}}$  over 1985–2021 along with a comparison to the pre-industrial state in the water column. The results over 36 years informed on the recent changes, inter-annual variations, and trends, but the time series appears somehow short to extrapolate the trends over time. What was the change of the carbonate system in surface waters before 1985 and what will be its future evolution?

#### 3.4.1 Back to the 1960s: observed trends since 1962

To explore the long-term change, we start by comparing our recent data with observations from the LUSIAD cruise conducted in 1962–1963 (Keeling and Waterman, 1968). Some data from this cruise were obtained in mid-November 1962 south of the polar front, in the region southwest off Kerguelen Islands. Because of the seasonality, we compared the November 1962 data with our observations obtained in October–November in 1995, 2011, and 2016 and with the FFNN model results for November (Fig. 13). The  $C_T$  concentration, pH,  $\Omega\text{Ar}$ , and  $\Omega\text{Ca}$  for 1962 were calculated using  $f\text{CO}_2$  data and  $A_T$  (from the  $A_T$ – $S$  relationship in Eq. 1) with salinity from the World Ocean Atlas (Antonov et al., 2006).

First, we note that the measured SST in November 1962 ( $1.7^\circ\text{C}$ ) was slightly lower compared to recent years (on average by about  $-0.6^\circ\text{C}$ ), but SST as low as  $1.8^\circ\text{C}$  for this season was also found in other years (e.g., November 1995, 2014). The change in SST is unlikely to explain the long-term increase in  $f\text{CO}_2$  or decrease in pH since 1962 (Fig. 13). In 1962, the oceanic  $f\text{CO}_2$  was  $324 \mu\text{atm}$ , which is slightly higher than in the atmosphere ( $\Delta f\text{CO}_2 = +8 \mu\text{atm}$ , a small source), whereas in November 1985–2020 the ocean was a small  $\text{CO}_2$  sink on average ( $\Delta f\text{CO}_2 = -3.3 \pm 4.5 \mu\text{atm}$ ). The  $C_T$  concentration in 1962 ( $2135 \mu\text{mol kg}^{-1}$ ) was much lower than observed since 1995, and the pH (8.115) was much higher than in the last 3 decades (Fig. 13). Compared to 1962, pH in 2016 was  $-0.078$  lower, i.e., representing 70 % of the pH decrease of  $-0.11$  in the global ocean since the beginning of the industrial era (Jiang et al., 2019). In November 1962, surface  $C_T$  was lower by  $-15.1 \mu\text{mol kg}^{-1}$  compared to the data in October 1995, i.e., a trend of  $+0.46 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$  over 33 years close to the  $C_{\text{ant}}$  trend observed in the WW over 1985–2021 as described above ( $+0.53 \pm 0.01 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$ ). Having the  $C_T$  value in 1962, we can project the  $C_T$  in time by adding

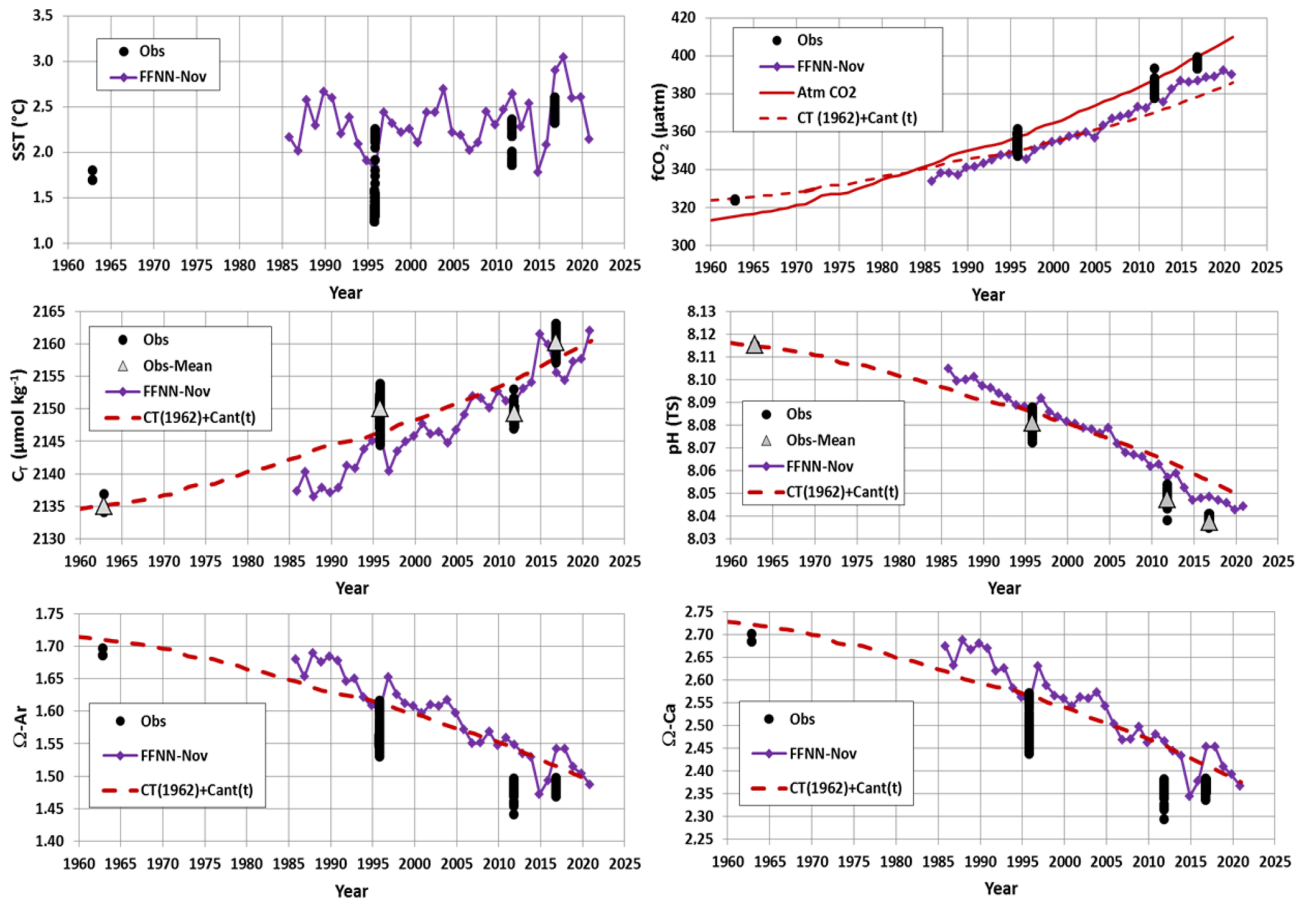


**Figure 12.** Profiles (0–400 m, left axis) of observed and calculated properties ( $C_T$ , pH,  $\Omega_{Ar}$ ,  $[CO_3^{2-}]$ ) at station OISO-KERFIX ( $50^{\circ}40' S$ – $68^{\circ}25' E$ ) in March 1985, January 2020, and January 2021 along with surface time series in 1985–2020 (right axis) of the same properties in January (yellow line) and August (blue line) from the FFNN model. The FFNN values in January 2020 are coherent with January 2020 or January 2021 observations in the mixed layer and in January 1985 are close to the observations in March 1985. Note that the differences of properties between 2020–2021 and 1985 have a similar magnitude as the seasonal amplitude (illustrated by the FFNN values for January and August).

the  $C_{ant}$  concentration based on the relationship observed between  $C_{ant}$  and atmospheric  $CO_2$  (Fig. 7b) assuming that the anthropogenic  $CO_2$  uptake since the 1960s is representative of the  $C_T$  change (i.e., the change of  $C_T$  due to natural variability was small). This projection is shown for all properties (dashed red lines in Fig. 13) and confirms that the progressive  $C_{ant}$  accumulation explained most of the  $C_T$  and  $fCO_2$  increase in surface waters since 1962. We note that the  $C_T$  derived from the FFNN model suggests slightly lower  $C_T$  compared to the  $C_{ant}$  projection especially before 2006. The difference of projected  $C_T$  and the FFNN model (on average  $-2.2 \pm 2.7 \mu mol kg^{-1}$ ) is within the uncertainty of  $C_T$  calculations (error is  $\pm 5 \mu mol kg^{-1}$  when using the  $A_T/fCO_2$  pairs), and the trend of the difference over 1985–2020 ( $-0.15 \mu mol kg^{-1} yr^{-1}$ ) is too small to be related with confidence to changes associated with natural

processes. On the other hand, the oceanic  $fCO_2$  recalculated with the projected  $C_{ant}$  trend suggested that for this season (November) the ocean moved from a  $CO_2$  source in 1962–1985 ( $\Delta fCO_2 > 0$ ) to a sink in 1986–2021 ( $\Delta fCO_2 < 0$ ) in line with results from the FFNN model. The recalculated  $fCO_2$  with  $C_{ant}$  (dashed red line in Fig. 13) was close to that observed in 1995 or from the FFNN model in 1985–2014 (mean difference over 1985–2014 is  $-1.2 \pm 5.2 \mu atm$ ). After 2016, the recalculated  $fCO_2$  suggests a stronger sink, and the difference with observations in 2011 and 2016 or the FFNN model is slightly higher (mean difference over 2016–2020 is  $-8.8 \pm 1.5 \mu atm$ ). Although the differences are in the range of the error in  $fCO_2$  calculation using  $A_T-C_T$  pairs ( $\pm 13 \mu atm$ ), this might indicate that after 2016 a process could contribute to increase  $fCO_2$  faster than the effect of  $C_{ant}$  only. This difference could be due to the warm-





**Figure 13.** Observed (black dots) sea surface temperature ( $^{\circ}\text{C}$ ),  $f\text{CO}_2$  ( $\mu\text{atm}$ ),  $\text{C}_T$  ( $\mu\text{mol kg}^{-1}$ ), pH (TS),  $\Omega\text{Ar}$ , and  $\Omega\text{Ca}$  around station OISO-KERFIX at  $50^{\circ}40' \text{S}$ – $68^{\circ}25' \text{E}$  for October–November. Also shown are the results for the FFNN model for November in 1985–2020 (purple). The  $\text{C}_T$  concentrations, pH,  $\Omega\text{Ar}$ , and  $\Omega\text{Ca}$  were calculated from  $f\text{CO}_2$  data using the  $A_T$ – $S$  relation (Eq. 1). The red line is the atmospheric  $f\text{CO}_2$ , and dashed red lines in each plot are the evolution of properties since 1960 corrected for  $\text{C}_{\text{ant}}$  where  $f\text{CO}_2$ , pH,  $\Omega\text{Ar}$ , and  $\Omega\text{Ca}$  were recalculated using  $\text{C}_T + \text{C}_{\text{ant}}$ ,  $A_T$  constant at  $2290 \mu\text{mol kg}^{-1}$ , and SST at  $2^{\circ}\text{C}$ . Grey triangles identify the mean values for  $\text{C}_T$  and pH.

ing that occurred after 2016 when SST was higher than 2 and up to  $3^{\circ}\text{C}$  in November 2017 (Figs. 13 and S9). The same could be applied for pH that was slightly lower than the pH recalculated from  $\text{C}_{\text{ant}}$  trend after 2015 (the mean difference between recalculated pH and FFNN-pH over 1985–2020 is only  $0.002 \pm 0.006$ ). Therefore, we conclude that for November the pH decrease since 1962 was mainly driven by the accumulation of anthropogenic  $\text{CO}_2$ . Aragonite and calcite saturation states also show a clear decrease since 1962 (Fig. 13), a diminution of 11 % over 59 years for both  $\Omega\text{Ar}$  and  $\Omega\text{Ca}$ . Based on these results over almost 60 years that confirm the conclusions from the observations in 1985–2021, we now evaluate the long-term change of the carbonate system in surface waters in the future.

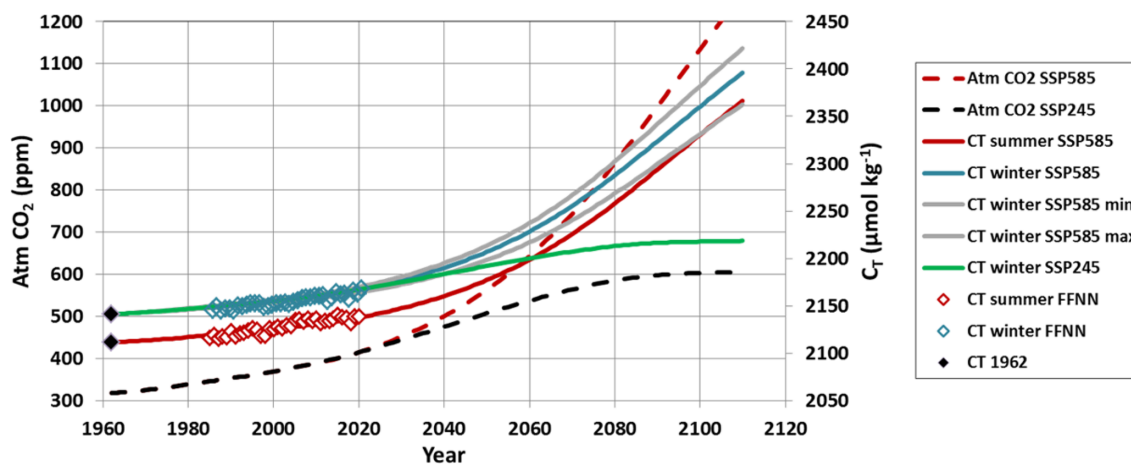
### 3.4.2 Projecting the observed trends in the future

The trends of the properties based on observations in 1962–2021 and the FFNN model in 1985–2020 indicate relatively

linear trends linked to  $\text{C}_{\text{ant}}$  uptake albeit with some decadal variability in summer (Fig. 4). A simple linear extrapolation of the trends in the future suggests that aragonite undersaturation in surface waters would be reached in year 2110 for the winter season and 2120 for summer (Fig. S17), whereas the subsurface trend suggests undersaturation in 2090. In year 2100, surface pH and  $[\text{H}^+]$  would be around 7.9 and  $12 \text{ nmol kg}^{-1}$  (Fig. S17). However, ESM CMIP6 models suggest that under a high emission scenario (SSP5-8.5), pH in 2100 in the Southern Ocean near  $50^{\circ}\text{S}$  would be around 7.65 and  $[\text{H}^+]$  around  $22 \text{ nmol kg}^{-1}$  (Jiang et al., 2023, their Fig. 4). This shows that the simple linear extrapolation based on recent observed trends (Fig. S17) underestimated the future change of the carbonate system for a high emission scenario as previously shown in the southeastern Indian Ocean based on summer trends derived from observations in 1969–2003 (Midorikawa et al., 2012, their Fig. 4).

**Table 3.** Results of the simulated properties for year 2020, 2050, and 2100 for two emission scenarios (SSP5-8.5 and SSP2-4.5). For 2020 the results based on observations in January (Obs.) and the FFNN model in January and August also listed. Sensitivity tests: “SSP85 W-T” is for winter with constant temperature, and “SSP85 W-A-T” is for winter with constant  $A_T$  and temperature.

Method	Year	Atm-CO <sub>2</sub> ppm	fCO <sub>2</sub> µatm	C <sub>T</sub> µmol kg <sup>-1</sup>	A <sub>T</sub>	pH TS	[H <sup>+</sup> ] nmol kg <sup>-1</sup>	[CO <sub>3</sub> <sup>2-</sup> ] µmol kg <sup>-1</sup>	ΩCa	ΩAr
Obs. Jan	2020	410.6	391.9	2142.2	2281.8	8.044	9.04	105.2	2.53	1.59
SD Obs.			(2.0)	(0.7)	(0.3)	(0.002)	(0.04)	(0.5)	(0.01)	(0.01)
FFNN Jan	2020	410.6	385.1	2138.5	2280.1	8.051	8.90	106.3	2.55	1.61
SSP summer	2020	414.9	375.4	2137.5	2282.1	8.061	8.70	108.0	2.60	1.63
FFNN Aug	2020	410.6	410.0	2168.3	2289.8	8.024	9.45	94.2	2.27	1.42
SSP winter	2020	414.9	434.5	2167.3	2282.1	8.001	9.98	90.4	2.18	1.37
SSP585 summer	2050	562.8	526.5	2177.2	2278.3	7.928	11.79	84.2	2.02	1.28
SSP585 winter	2050	562.8	624.7	2207.0	2278.3	7.857	13.91	68.5	1.65	1.04
SSP585 W-A-T	2050	562.8	585.7	2207.0	2280.0	7.880	13.17	69.0	1.66	1.04
SSP585 W-T	2050	562.8	592.7	2207.0	2278.3	7.875	13.32	68.1	1.64	1.03
SSP245 winter	2050	506.9	554.8	2192.0	2278.3	7.905	12.46	75.8	1.92	1.15
SSP585 summer	2100	1135.2	1986.9	2330.6	2271.8	7.394	41.31	26.9	0.65	0.41
SSP585 winter	2100	1135.2	2306.3	2360.4	2271.8	7.316	48.26	21.8	0.52	0.33
SSP585 W-A-T	2100	1135.2	1993.1	2360.4	2280.0	7.372	42.44	22.6	0.54	0.34
SSP585 W-T	2100	1135.2	2097.0	2360.4	2271.8	7.349	44.74	21.3	0.51	0.32
SSP245 winter	2100	602.8	753.9	2217.7	2271.8	7.782	16.51	60.9	1.47	0.92



**Figure 14.** Evolution of atmospheric CO<sub>2</sub> (ppm) and sea surface C<sub>T</sub> (µmol kg<sup>-1</sup>) between 1960 and 2110 evaluated for two scenarios (SSP2-4.5 dashed black and SSP5-8.5 dashed red), for summer (red line for SSP5-8.5) and winter (blue line for SSP5-8.5 and green line for SSP2-4.5). Grey lines are the high and low C<sub>T</sub> for winter SSP5-8.5 based on the error in the C<sub>ant</sub>/fCO<sub>2</sub> relationship (Fig. 7b). Also shown are the results for the FFNN model in 1985–2020 for summer (red diamonds) and winter (blue diamonds) and C<sub>T</sub> in 1962 (black diamonds). The C<sub>T</sub> values for different seasons and scenarios were used to calculate the carbonate properties in the future (Fig. 15).

To better investigate the changes for the next decades, we assumed that the C<sub>ant</sub> trend for the modern period (Fig. 7) that experienced a “business as usual” scenario after the 1960s is representative of the future changes in the surface ocean carbonate system. For this analysis, we used two emissions scenarios (shared socioeconomic pathways, SSPs; Meinshausen et al., 2020) with atmospheric xCO<sub>2</sub> reaching 1135 ppm in 2100 (a “high” emission scenario SSP5-8.5) or xCO<sub>2</sub> reaching 603 ppm in 2100 after a stabilization

around 2080 (scenario SSP2-4.5). This enables us to simulate future C<sub>T</sub> concentrations for summer or winter (Fig. 14) and to calculate other carbonate properties using C<sub>T</sub> and A<sub>T</sub> (Fig. 15, Table 3) in response to approximated future changes in physical and geochemical properties excluding impacts of changes in atmospheric and oceanic circulation. As the calculated properties are sensitive to A<sub>T</sub> values, we used a fixed A<sub>T</sub> of 2280 µmol kg<sup>-1</sup> or applied a correction based on the long-term change of sea surface salinity observed in the last

6 decades (1960–2017), i.e., a freshening in the Southern Ocean of around  $-0.01$  to  $-0.02$  per decade (Durack and Wijffels, 2010; Cheng et al., 2020b). The decrease in salinity in the southern Indian Ocean ( $-0.02 \pm 0.01$  per decade) was recently analyzed by Akhondas et al. (2023), who showed that in the years 1993–2021 the freshening was mainly due to an increase in precipitation linked to the acceleration of the atmospheric hydrological cycle. From our data in the mixed layer over 1985–2021, we estimated a trend in salinity of  $-0.021 \pm 0.004$  per decade. For the  $A_T$  sensitivity test, we thus selected a salinity trend of  $-0.01$  per decade in 1962–1985 and  $-0.02$  per decade after 1985 and applied these trends to simulate  $A_T$  over 1960–2100 using the  $A_T$ –salinity relationship (Eq. 1). This leads to a salinity of 33.650 and  $A_T$  of  $2272 \mu\text{mol kg}^{-1}$  in the year 2100, about  $8 \mu\text{mol kg}^{-1}$  lower than observed in 2021 ( $2280 \mu\text{mol kg}^{-1}$ ). Compared to the  $C_T$  change from 2021 to 2100 ( $+50$  and  $+193 \mu\text{mol kg}^{-1}$  for the “low” and “high” emissions scenario, Fig. 14), the impact of the  $A_T$  decrease has a minor effect on the future change for pH,  $[\text{CO}_3^{2-}]$ , and  $\Omega$  (Table 3). For example, in winter for the SSP5-8.5 scenario, when the  $A_T$  decrease is taken into account, pH in 2100 is 7.316 and  $\Omega_{\text{Ar}}$  is 0.33 against 7.372 and 0.34 when  $A_T$  is constant (Table 3). In both cases, the surface aragonite undersaturation ( $\Omega_{\text{Ar}} = 1$ ) in winter occurred in 2055, whereas in summer it is identified in 2070. The effect of lower  $A_T$  in the future appeared also small compared to the seasonal differences of pH and  $\Omega$  in 2100.

As noted above, the Southern Ocean experienced a warming in recent decades (e.g., Auger et al., 2021), and it is projected that warming will continue in the future (IPCC, 2022). Therefore, to test the sensitivity of calculated properties to warming we applied a warming of  $+0.0125 \text{ }^\circ\text{C yr}^{-1}$  in 1985–2020 and  $+0.025 \text{ }^\circ\text{C yr}^{-1}$  after 2020 (Azarian et al., 2023). As for  $A_T$ , these results are compared for winter using constant SST (Table 3). The effect of the long-term warming does mainly impact the projection of  $[\text{H}^+]$  and pH (Table 3).

These sensitivity tests for temperature and  $A_T$  showed that as for the observed period 1962–2021 (Fig. 13), the projection in the future depends mainly on the anthropogenic  $\text{CO}_2$  accumulation. Here, the  $C_T$  concentrations were calculated using the  $C_{\text{ant}}$  versus atmospheric  $\text{CO}_2$  relationship (Fig. 7b). We thus tested the results for winter based on the error associated with this relationship (Fig. S18). This leads to either higher or lower  $C_T$  compared to the original calculation (Fig. 14). For the SSP5-8.5 scenario, the winter  $C_T$  concentrations in 2100 range between 2328 and  $2378 \mu\text{mol kg}^{-1}$ , higher than simulated in the ESM CMIP6 models around  $50^\circ \text{S}$  ( $2300 \mu\text{mol kg}^{-1}$ ; Jiang et al., 2023). As in the ESMs, the projected  $C_T$  concentration in 2100 at our location for the SSP2-4.5 scenario is much lower,  $2217 \mu\text{mol kg}^{-1}$  (Fig. 14). The future change of the carbonate system is not significantly different using low or high  $C_{\text{ant}}$  accumulation (Fig. S18), but this test gives a range of years to reach aragonite and calcite undersaturation. In winter (SSP5-8.5 scenario), aragonite (calcite) would reach undersaturation between year 2050

and 2060 (between year 2070 and 2080). Note that for summer we derived undersaturation for  $\Omega_{\text{Ar}}$  in year 2065 and for  $\Omega_{\text{Ca}}$  in year 2085. For the SSP2-4.5 scenario, where  $C_T$  is  $143 \mu\text{mol kg}^{-1}$  lower in 2100 compared to SSP5-8.5, aragonite undersaturation would not be reached before 2070 (Fig. 15).

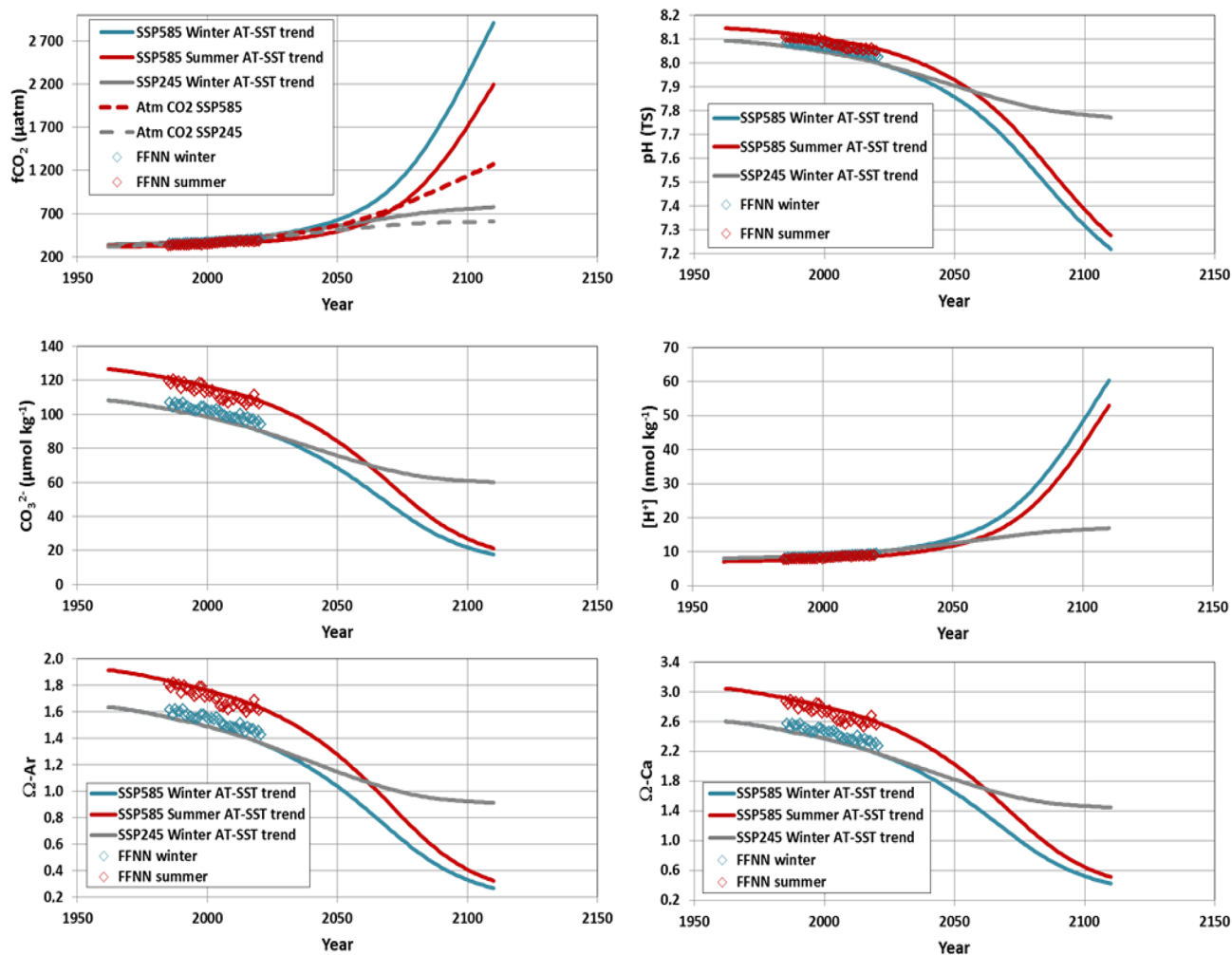
#### 4 Summary and concluding remarks

The times series of high-quality observations collected between 1985 and 2021 and the results from the FFNN model at one location, south of the polar front in the southern Indian Ocean ( $50^\circ \text{S}$ – $68^\circ \text{E}$ ), presented in this analysis offered new results on the inter-annual variability, decadal to long-term trends of the carbonate system in surface waters, air–sea  $\text{CO}_2$  fluxes, and associated drivers. The evaluation of anthropogenic  $\text{CO}_2$  concentrations in the water column indicated that the trends of the carbonate species are mainly driven by the anthropogenic  $\text{CO}_2$  uptake leading to a progressive acidification in surface waters and at depth.

In 1985, the  $C_{\text{ant}}$  concentrations were approaching  $50 \mu\text{mol kg}^{-1}$  at 200 m, and  $C_{\text{ant}}$  was detected in the water column down to the bottom (1600 m). This explains why aragonite undersaturation was observed at 600–700 m in 1985, where  $[\text{CO}_3^{2-}]$  concentration was at its minimum, whereas for the pre-industrial era the whole water column was super-saturated (this study Fig. S15; Lauvset et al., 2020, their Fig. S15). Because of the anthropogenic  $\text{CO}_2$  accumulation, 36 years later, we observed an upward migration of the aragonite saturation horizon that was found around 400 m in 2021 (a shoaling rate of around  $-6 \text{ m yr}^{-1}$ ).

At the subsurface, in the winter water layer, the  $C_{\text{ant}}$  trend is estimated at  $+0.53 \pm 0.01 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$  over 1985–2021 with a detectable increase of the trend in recent years. The  $C_{\text{ant}}$  concentrations in the ocean are closely related to the atmospheric  $\text{CO}_2$  concentrations, and the slope we observed south of the PF in the Indian sector of  $+0.263 \pm 0.042 \mu\text{mol kg}^{-1} \mu\text{atm}^{-1}$  is close to that observed in the AAIW in the South Atlantic (Fontela et al., 2021). This suggests that local observations in the southern Indian POOZ captured the link between  $C_{\text{ant}}$  and atmospheric  $\text{CO}_2$  at a larger scale.

In surface waters, over 1991–2020 the oceanic  $f\text{CO}_2$  increased at a rate close to or slightly lower than in the atmosphere (Fig. 2b), and the  $C_T$  trend followed the  $C_{\text{ant}}$  accumulation (Figs. 4b, S12a). However in the last decade both observations and the FFNN model showed low  $f\text{CO}_2$  trends in summer (less than  $1 \mu\text{atm yr}^{-1}$ ). The change in summer trend appears related to primary production as revealed by a decrease of Chl *a* in 1998–2010 followed by an increase after 2010. Biological activity counteracts the  $C_T$  increase due to  $C_{\text{ant}}$ , resulting in rather stable  $C_T$  and  $f\text{CO}_2$  in summer during the last decade. As a result, the region moved from an annual source of  $+0.8 \text{ mol C m}^{-2} \text{ yr}^{-1}$  in 1985 to



**Figure 15.** Evolution of sea surface  $f\text{CO}_2$  ( $\mu\text{atm}$ ), pH (TS),  $[\text{CO}_3^{2-}]$  ( $\mu\text{mol kg}^{-1}$ ),  $[\text{H}^+]$  ( $\text{nmol kg}^{-1}$ ),  $\Omega_{\text{Ar}}$ , and  $\Omega_{\text{Ca}}$  between 1960 and 2110 evaluated for the SSP5-8.5 scenario for winter (blue line) and summer (red line) taking into account both  $A_{\text{T}}$  and SST future trends. For winter the results are also presented using the SSP2-4.5 scenario (grey lines). Also shown are the results for the FFNN model in 1985–2020 for summer (red diamonds) and winter (blue diamonds). Atmospheric  $f\text{CO}_2$  is also shown for SSP5-8.5 (dashed red) and SSP2-4.5 (dashed grey). Values in 2020, 2050, and 2100 for different sensitivity tests are listed in Table 3.

a sink of  $-0.5 \text{ molC m}^{-2} \text{ yr}^{-1}$  in 2020. Adding historical data from November 1962 that indicate an annual source of  $2.2 \text{ molC m}^{-2} \text{ yr}^{-1}$  and extrapolating to the entire southern Indian POOZ ( $50\text{--}58^\circ \text{ S}$ ,  $20\text{--}120^\circ \text{ E}$ ;  $6.5 \text{ M km}^2$ ) suggest that this region changed from a  $\text{CO}_2$  source of  $0.17 \text{ PgC yr}^{-1}$  in 1962, reduced to  $0.06 \text{ PgC yr}^{-1}$  in 1985, to a  $\text{CO}_2$  sink of  $-0.04 \text{ PgC yr}^{-1}$  in 2020. This can be compared with reconstructed fluxes from a data-based model that produced a  $\text{CO}_2$  source around  $0.10 \text{ PgC yr}^{-1}$  in 1960–1990 and a sink around  $-0.05 \text{ PgC yr}^{-1}$  in 2020 in the southern Indian sector (Rödenbeck et al., 2022, their Fig. 6). Based on the FFNN reconstructions, the increase of the ocean  $\text{CO}_2$  sink was particularly pronounced after 2011 (Fig. 3) when phytoplankton biomass was increasing in this HNLC region and occurred when the SAM index was in a positive state. Although observations in the water column do not suggest enhanced up-

welling, we cannot eliminate the possibility that the SAM influenced changes in primary production.

For October/November, the estimated increase in  $C_{\text{T}}$  concentration in surface waters over 54 years ( $+21 \mu\text{mol kg}^{-1}$ ) was almost equal to the increase of  $C_{\text{ant}}$  ( $+22.3 \mu\text{mol kg}^{-1}$ ). As a result, surface ocean pH dropped from 8.11 in 1962 to 8.044 in 2020. Over a multi-decadal timescale (30 years or more), acidification in the southern Indian POOZ was mainly controlled by the uptake of anthropogenic  $\text{CO}_2$ . However, our data also indicate a modulation of the summer pH trend by natural processes. After 2010, a very small pH trend was estimated in summer ( $-0.0098 \pm 0.0042$  per decade) when the region experienced an increase in primary productivity. On the opposite, in winter, the pH trends continuously increased with time. At the subsurface (winter water layer), the trend of pH based on  $A_{\text{T}}$  and  $C_{\text{T}}$  data over 1985–2021

( $-0.0161 \pm 0.0033$  per decade) is also almost equal to the annual surface trend from the FFNN model. A simple extrapolation of the trends in the WW indicated that undersaturation ( $\Omega < 1$ ) would be reached at year 2090 for aragonite and year 2180 for calcite. However, as atmospheric  $\text{CO}_2$  is expected to increase and ocean  $C_T$  will increase in the future, pH and  $\Omega$  will decrease at a faster rate than observed in the last decades. A projection of future  $C_T$  concentrations based on two emission scenarios, excluding changes in ocean circulation, indicated that the winter surface pH in 2100 would decrease to 7.32 for a high emission scenario (SSP5-8.5) or to 7.782 for a low emission scenario (SSP2-4.5). This is up to  $-0.86$  lower than pre-industrial pH and  $-0.71$  lower than pH observed in 2020. For the winter season the aragonite undersaturation in surface would be reached around 2050 for a high emission scenario and 2070 for a low emission scenario.

The time series presented here for the Southern Ocean, along with other historical time series of  $A_T$  and  $C_T$  in the water column (BATS, HOT, ESTOC, KNOT, Iceland, or Irminger seas; Bates et al., 2014; Lange et al., 2024) or the recent BGC-Argo floats in the Southern Ocean (Mazloff et al., 2023), offer useful data for the evaluation of biogeochemical and Earth system models, especially for the physical and biological drivers of the carbonate system not well represented in current models at seasonal to decadal scales in the Southern Ocean (e.g., Hauck et al., 2023a; Rodgers et al., 2023; Joos et al., 2023). Observing the decadal changes of the carbonate system in the water column is also an important step to extend the evaluation of biogeochemical and ESMs below the surface (Jiang et al., 2023). It is important to maintain such time series for monitoring the future evolution of the ocean  $\text{CO}_2$  sink, of the acidification, and its impact on phytoplankton species and higher trophic levels. This is especially the case in marine protected areas such as the French sub-Antarctic islands including the Kerguelen Archipelago, which was listed as a UNESCO World Heritage Site in 2019.

**Data availability.** Data used in this study are available in SOCAT (<https://doi.org/10.25921/1h9f-nb73>, Bakker et al., 2022) for  $f\text{CO}_2$  surface data, in GLODAP (<https://doi.org/10.25921/ttq-n825>, Lauvset et al., 2021b) for water-column data, and at NCEI/OCADS ([https://doi.org/10.3334/cdiac/otg.carina\\_35mf19980121](https://doi.org/10.3334/cdiac/otg.carina_35mf19980121), Lo Monaco and Metzl, 2013). The CMEMS-LSCE-FFNN model data are available at EU Copernicus Marine Service Information (<https://doi.org/10.48670/moi-00047>, Chau et al., 2023).

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**Author contributions.** CLM and NM are co-PIs of the ongoing OISO project. CLM, NM, CL, and CR participated in OISO cruises. Underway  $f\text{CO}_2$  was measured by CLM, NM, and CL and qualified by CLM and NM. Nutrient data were measured and qualified

by CLM and CL. Chl-*a* data were measured and qualified by CR. Water column data were qualified by CLM, NM, CL, CR, and GR. MG, FC, and TTTC developed the CMEMS-LSCE-FFNN model and provided the model results. NM started the analysis, wrote the draft of the manuscript, and prepared the figures. All authors contributed to revising the draft manuscript.

**Competing interests.** The contact author has declared that none of the authors has any competing interests.

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