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Interannual variability of carbon dioxide drawdown by subantarctic surface water near New Zealand

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Abstract The ocean-atmosphere flux of carbon dioxide in subantarctic surface water (SASW) east of New Zealand has been determined using data from bi-monthly cruises on a time series transect for 8 years. The 60 km long transect extends from the coast (45.770°S 170.720°E) to a station at 45.833°S 171.500°E. Sea surface temperature, salinity, nutrient concentrations and pCO_2 have been measured at a frequency of about once every 2 months from January 1998 until December 2005. Measured pCO_2 exhibits a seasonal cycle with a maximum in late winter/spring, and a minimum in late summer/autumn, a mean 356 µatm, and an amplitude of 9 µatm. The magnitude of ΔpCO_2 (the air-sea concentration gradient) has increased over the 8 years, primarily due to the increase in atmospheric CO_2 concentration. The air-sea flux of CO_2 was determined from wind speed data and ΔpCO_2. The uptake of atmospheric CO_2 by SASW in the study area changed from + 1 and +82 mmol m^{-2} in 1998 and 1999 respectively (ocean as source) to −870 and −510 mmol m^{-2} in 2004 and 2005 (ocean as sink). These values are substantially less in magnitude than the value obtained from the Takahashi et al. (Deep-Sea Res II, 2009) flux climatology.

Keywords pCO_2 · Subantarctic surface water · New Zealand · Air-sea CO_2 flux

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Introduction

The Southern Ocean has been identified as a sink for carbon dioxide although there is disagreement on the magnitude and relative importance of the sink (Gurney et al. 2002; Le Quere et al. 2007; Lo Monaco et al. 2005; McNeil et al. 2007; Mikaloff-Fletcher et al. 2007; Murnane et al. 1999; Orr et al. 2001; Tans et al. 1990). Undersaturation of surface water pCO_2, high wind speeds, several frontal zones and large surface area combine to give the conditions required for high negative air-sea carbon fluxes in this area. Takahashi et al. (2009) calculate the net sea-air flux of CO_2 in the Southern Ocean (defined by those authors as south of 50°S) for the reference year 2000 to be -0.05×10^{15} g C $year^{-1}$, accounting for 4% of the total global oceanic uptake. This is significantly less than the flux estimated using the earlier database (Takahashi et al. 2002) due to the increased number of measurements available, however the

pCO_2 data upon which these values are based are still relatively sparse in terms of both space and time due to the difficulty of sampling in the inhospitable environment of the Southern Ocean, particularly in winter.

Direct measurements of pCO_2 in surface waters of the Indian Ocean sector of the Southern Ocean identified this area as a sink for atmospheric CO_2 in summer (Goyet et al. 1991; Inoue and Sugimura 1988; Metzl et al. 2006, 1999; Poisson et al. 1993; Robertson and Watson 1992). Similarly, the Atlantic Ocean (Schneider and Morlang 1995; Takahashi et al. 1993) and Pacific Ocean (Morrison et al. 2001; Sabine and Key 1998) sectors were sink areas in the austral summer. However, the high spatial heterogeneity of biogeochemical processes arising from primary productivity in the austral summer results in difficulties in extrapolating measured pCO_2 to a regional scale (Metzl et al. 2006).

There are few winter measurements of pCO_2 in the Southern Ocean. Several studies however (Gibson and Trull 1999; Goyet et al. 1991; Metzl et al. 1991; Murphy et al. 1991; Rubin et al. 1998), indicate that the Southern Ocean is a lesser sink in the austral winter than in the summer, and that some areas may act as small sources of atmospheric carbon dioxide.

The distribution of carbon in high southern latitudes is generally not well modelled by global ocean carbon models, with disagreement on the location and magnitude of the Southern Ocean sink areas (Gurney et al. 2002; Mikaloff-Fletcher et al. 2007; Sabine and Key 1998). This is partly due to the incomplete understanding of the factors and processes controlling the carbon dioxide chemistry in this region of the ocean.

Data from well-established time series stations in other areas such as Station P in the north–east Pacific Ocean (Wong and Chan 1991), Bermuda Atlantic Time-series Study (BATS) in the western North Atlantic Ocean (Bates et al. 1996; Gruber et al. 2002), Hawaii Ocean Time-series (HOT) in the central Pacific Ocean (Brix et al. 2004; Dore et al. 2003; Keeling et al. 2004; Winn et al. 1998) and ESTOC in the subtropical north Atlantic Ocean (González-Dávila et al. 2003; Santana-Casiano et al. 2007) indicate the highly variable nature of the marine carbon cycle and thus the importance of having observations which allow determination of seasonal and interannual variability.

This paper reports a time-series study of the CO_2 chemistry of subantarctic surface water (SASW) in the southwest Pacific Ocean sector of the Southern Ocean. The 8 year long data record allows examination of both the seasonal and interannual variability of the uptake of atmospheric carbon dioxide by the SASW in this region.

Characteristics of southwest Pacific oceanography

Subantarctic surface water is the Southern Ocean surface water mass bounded by the subantarctic front (SAF) to the south, and the subtropical front (STF) to the north, occupying approximately the latitude band 40–50°S (Heath 1981). Metzl et al. (1999) present fCO_2 data from the Indian sector of the SASW (termed SAZ by those authors) and extract monthly measurements which show a clear seasonal signal with a minimum in the austral summer and a late winter maximum. Metzl et al. (1999) estimate that the subantarctic waters in the Indian Ocean Sector are a strong sink for atmospheric carbon dioxide, particularly in summer. Compiling the Indian Ocean data with measurements made in the Atlantic and Pacific Oceans, Metzl et al. (1999) estimate that the annual flux is 1 PgC $year^{-1}$ for the entire circumpolar SASW. Deep penetration of anthropogenic carbon dioxide has occurred in the SASW south of Australia (McNeil et al. 2001), and extrapolation of the atmospheric CO_2 uptake to the entire SASW gives a value of 0.73–0.86 PgC $year^{-1}$. A significant depletion in atmospheric carbon dioxide near Cape Grim, Tasmania, Australia, has been attributed to the subantarctic sink (Monfray et al. 1996). Data from four (austral) summer cruises in the Southern Ocean south of Australia showed that both the temporal and spatial variation of pCO_2 in the Subantarctic Water are related to seawater temperature (Yoshikawa-Inoue and Ishii 2005). In the low chlorophyll subantarctic surface waters south of New Zealand, pCO_2 was primarily controlled by mixing processes (Rangama et al. 2005), however interannual variability in this area is large. A long term increase of pCO_2 in the Subantarctic Zone of $+1.0 +/- 0.5$ μatm $year^{-1}$ was determined, and attributed to

the uptake of anthropogenic CO_2, ocean transport and biological activity, however large interannual/decadal variation were superimposed on the long term increase (Rangama et al. 2005; Yoshikawa-Inoue and Ishii 2005).

The New Zealand land mass interrupts the circumglobal STF, and therefore SASW is located to the south and east of the South Island of New Zealand (Fig. 1). The physical oceanography of SASW in the vicinity of New Zealand has been well described (Burlington 1961; Butler et al. 1992; Chiswell 1996; Chiswell 2002; Hamilton 2006; Heath 1972; Heath 1981; Heath 1985; Jillett 1969; Morris et al. 2001; Sutton 2003). Subantarctic water, like other Southern Ocean water masses, is generally high in nutrient concentration (Bradford and Taylor 1980) and low in chlorophyll concentration (Vincent et al. 1991), and this has implications for ecosystem structure and function (Bradford-Grieve et al. 1999). Subantarctic waters are known to be iron limited (Boyd et al. 2002). Iron/light co-limitation in spring and iron/silicic acid co-limitation in summer affect algal growth in subantarctic waters (Hutchins et al. 2001; Sedwick et al. 2002).

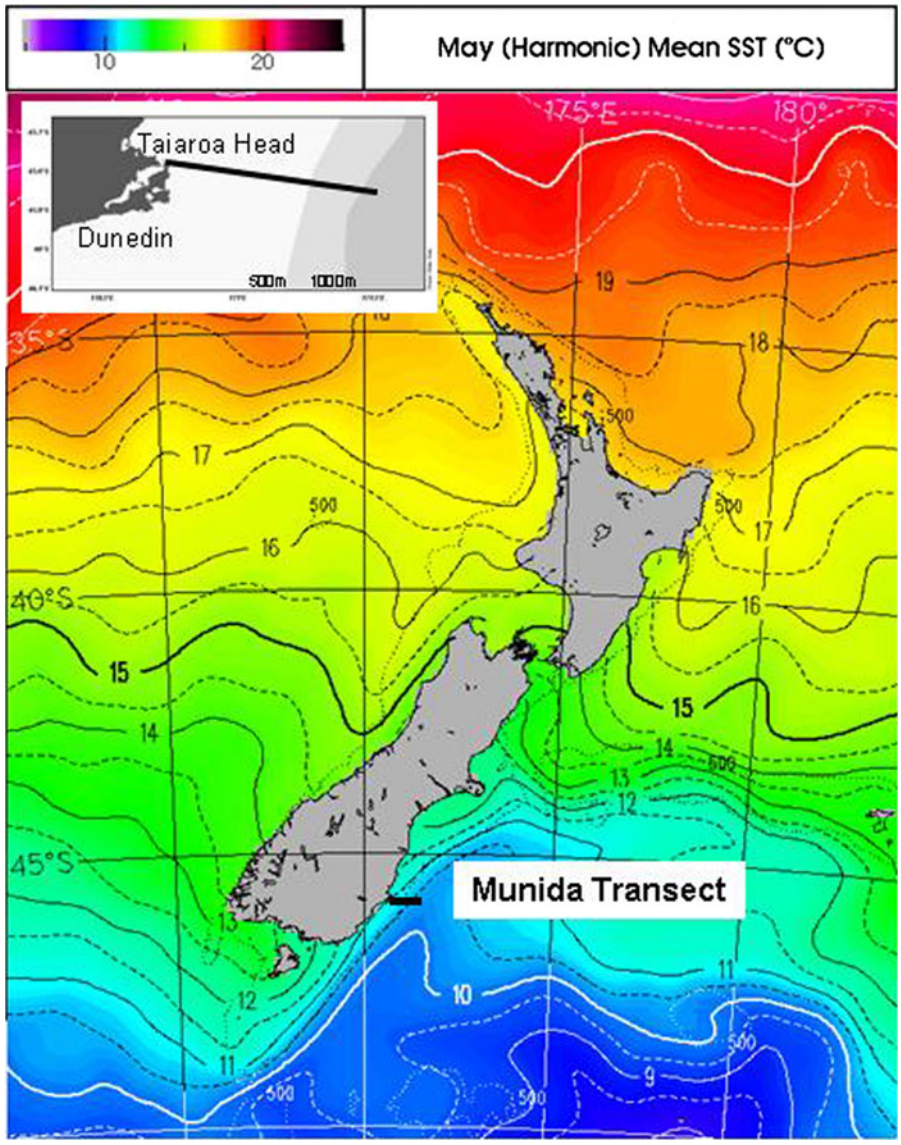

Fig. 1 Location of the study site, *the contours* indicate sea surface temperature, May climatology (NIWA SST Archive). The subtropical front (STF) is coincident with the 10.5°C isotherm in the region of the study site, subantarctic surface water is south and east of the STF. The *insert* is a close-up of the transect location

Study area

The time series transect has been established off the east coast of the South Island of New Zealand (Fig. 1). The 60 km long transect runs from Taiaroa Head at the tip of the Otago Peninsula (45.770°S 170.720°E) offshore in an east-southeasterly direction to a station at 45.833°S 171.500°E, and is based on the transect studied by Jillett (1969). The transect crosses through neritic water (typically 0–15 km offshore), the modified subtropical water of the Southland Current (15–40 km offshore), the STF and SASW (> 45 km offshore). 50 sampling trips have been made in the 8-year period from January 1998 to December 2005 as part of an on-going programme. Continuous temperature, salinity and pCO_2 measurements are made routinely, in addition to which discrete samples are taken at surface stations, two of which are in located in the subantarctic water portion of the transect. These are analysed for total alkalinity (A_T) and concentrations of dissolved reactive phosphate, silicate, nitrate and chlorophyll a. The transect has been termed the Munida transect, named after the vessel (*RV Munida*) used during the sampling voyages. Ohline et al. (2007) have previously reported the pH results from the Munida transect, and have evaluated the quality of pCO_2 determined from measured pH and alkalinity.

Satellite SST images (Uddstrom and Oien 1999) clearly show the position of the STF in the vicinity of the transect as a region of high temperature gradient. The equi-temperature water mass eastward of the front is SASW and extends well beyond the 171.500°E position marking the end of the transect (Fig. 1). On three occasions it has been possible to extend the length of the transect further to the east into subantarctic water using a larger vessel. No noteworthy variation in temperature or salinity was observed up to distances of 220 km beyond the end of the transect, indicating that SASW at the location of the Munida transect is similar to that further offshore.

Methods

Seasurface water temperature and conductivity were measured from January 1998 to October 2000 using a SBE 19-03 Seacat Profiler from Sea-Bird Electronics, Inc, then from October 2000 onward using a SBE21 thermosalinograph from Sea-Bird Electronics, Inc. The SBE instruments are returned to the manufacturer for calibration and maintenance on a bi-annual basis. The accuracy of the sea surface temperature measurements is taken as ±0.1°C.

Surface water pCO_2 was measured continuously using an equilibration system with infrared analysis similar to that described by Kortzinger et al. (1996). Surface seawater was taken from the ship's supply, sampled at 2 m depth. The water continuously flowed through an equilibration chamber which was vented to the atmosphere thus maintaining atmospheric pressure in the equilibration chamber headspace. A closed volume of air was bubbled through the constantly-renewed seawater sample in the equilibration chamber, allowing gas–liquid exchange of carbon dioxide to occur. The equilibrated gas circulated through a series of valves, a pump, chemical drying column, mass flow controller, and infrared gas analyser (LiCor CO_2 analyser, model LI-6251) before re-entering the equilibration chamber via a glass frit. The design of the equilibration chamber ensured that the headspace was at atmospheric pressure (P_{atm}). pCO_2 in the equilibration chamber was calculated from the measured mole fraction of CO_2 in dry air (XCO_2) using Eq. 1.

$$pCO_2 = XCO_2(P_{atm} - p_{sw}) \quad (1)$$

where p_{sw} is the seawater vapour pressure, calculated using the equation of Weiss (1974). The temperature in the equilibration chamber was measured using a calibrated thermistor, the accuracy of which is estimated to be ±0.1°C. pCO_2 at the sea surface temperature is required for in-situ calculations and comparisons, therefore the change in pCO_2 caused by any temperature increase which occurred during the measurement process was corrected for using the polynomials derived by Copin-Montegut (1988, 1989).

The infrared gas analyser, operated in absolute mode, was calibrated at the beginning and end of each cruise while en route to/from the transect (intercalibration interval approximately 8 hours) using CO_2-in-air secondary standards calibrated by NIWA's Atmospheric Trace Gas Laboratory, and based on the X95 scale of the then-WMO Central Calibrating Laboratory (Scripps Institution of Oceanography UCSD). At-sea calibration involved

a standard gas close in concentration to the atmosphere, therefore close to, but not always greater than the seawater value, and a zero-CO_2 standard, generated by passing ambient air through a soda lime trap. The third-order calibration polynomial was determined in the laboratory using 3 standard gases plus a zero-standard, with the highest standard being greater than the measured seawater values (406.8 ppm). The pressure and temperature in the infrared cell was measured, and explicitly included in the calculation of mole fraction from voltage (LI-COR 1998). Instrument drift (typically less than 1.5 µatm/calibration period) was corrected for by assuming that any drift at the CO_2 of each standard was linear between each calibration. The uncertainty of the pCO_2 measurements is estimated to be 1.5%, based on participation in an international intercomparison experiment (Nojiri 2003), and taking into account uncertainties in the measurement of sea surface temperature.

Filtered (Whatman GF/F) nutrient (dissolved reactive phosphate and silicate, and nitrate) samples were collected in acid-washed HDPE bottles and stored frozen until analysis. Nutrient samples were analysed colorimetrically using an Pertorp Analytical Alpchem Autoanalyser (method 00629) for the period January 1998 to October 2001 and an Astoria Pacific API 300 micro segmented flow analyser with digital detector (EPA method 365.5) for the period October 2001 onwards.

Results

The surface data is calculated as a function of distance offshore (0 km = 45.770°S 170.720°E). An example of sea surface temperature, salinity and pCO_2 data from the surface transect, taken in September 2005, is shown in Fig. 2. A temperature change from 10.8 to 8.5°C, and a salinity change from 34.7 to 34.4 psu marks the STF at 35–42 km offshore. Eastward of the STF, at distances greater than 50 km offshore, the SASW has a sea surface temperature of 8.5°C and a salinity of 34.4 psu. The pCO_2 surface profile shows an increase in pCO_2 from 265 to 280 µatm in the subtropical water to 360 µatm in the SASW. Often the STF is not as evident as on this occasion, particularly in summer when warming of the surface waters can lead to spreading of the

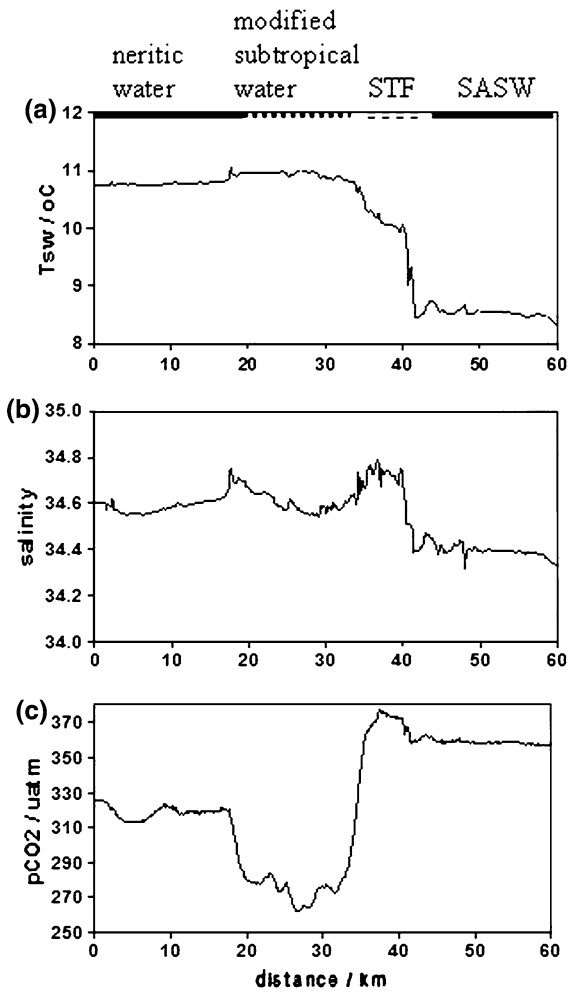

Fig. 2 Horizontal profiles of **a** sea surface temperature, **b** sea surface salinity and **c** pCO_2 for 14 September 2005. The location of the water masses are marked on the *top panel*

SASW over the sub-tropical water, blurring the front at the surface.

The complete dataset of surface temperature data is are shown in the form of a contour plot in Fig. 3a. The temperature values range from a minimum of 7.5°C in SASW in winter to greater than 16.5°C in neritic water in summer of some years. The seasonal cycle of warm water in the (austral) summer and cooler water in the (austral) winter can be seen in all water types, and the SASW is always cooler than the adjacent water of subtropical origin. The salinity data is shown in a similar format in Fig. 3b. The SASW is characterised by low salinity of 34.3. The pCO_2 data (Fig. 3c) is somewhat harder to interpret, as expected from a parameter that is affected by many factors,

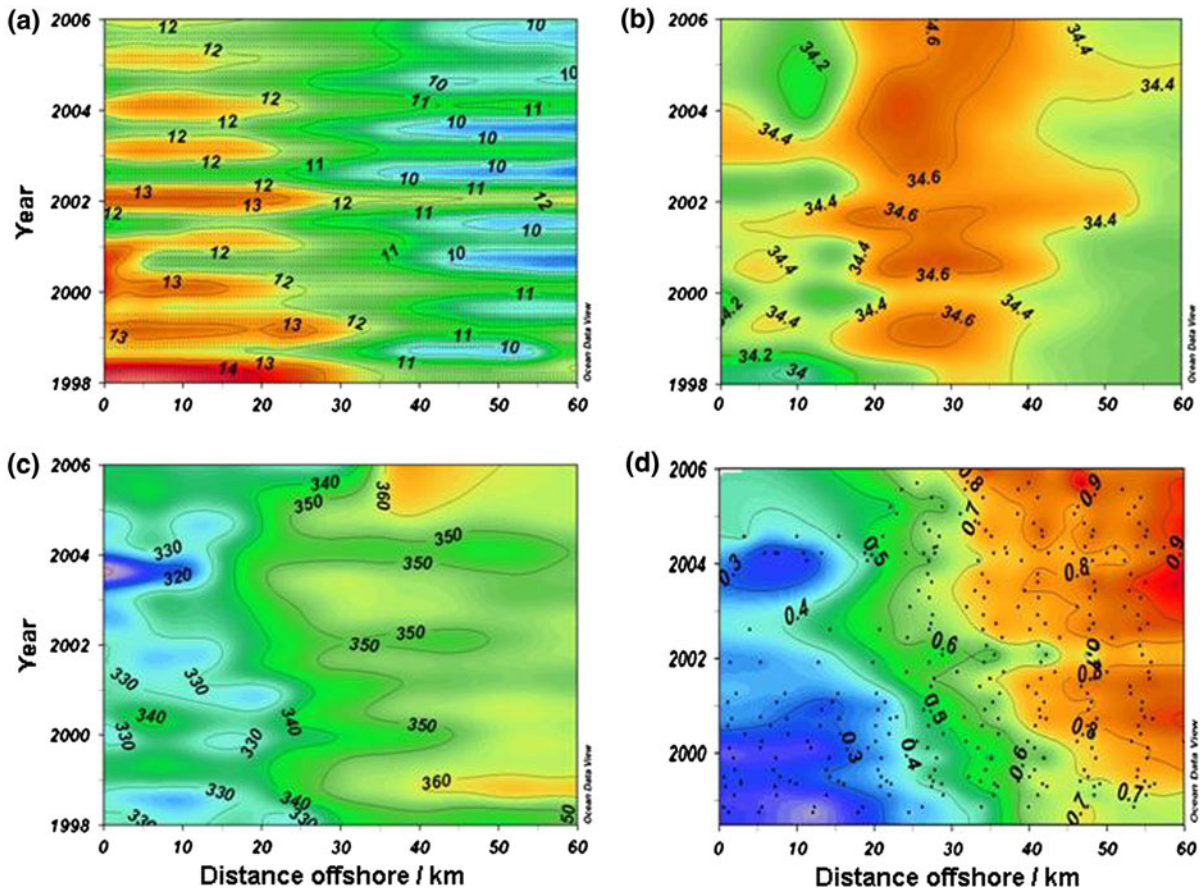

Fig. 3 Sea surface **a** temperature, **b** salinity, **c** pCO_2 and **d** dissolved reactive phosphate concentration from the Munida transect shown as *contour maps*. The sampling times are indicated by *black dots* in plot (**d**)

however some broad trends can be noted. In general, pCO_2 is higher in offshore waters. A seasonal cycle of lower values in spring, higher in autumn occurs in neritic water, whereas in the Southland Current and SASW the pCO_2 is higher in late spring/summer and lower in winter. Values range from as low as 215 µatm in neritic water in August 2001 to a maximum of 380 µatm in August 1999 and July 2005.

Currie and Hunter (1998) identified two scenarios describing pCO_2 variation in this region in 1992/1993. In winter and spring, pCO_2 increased from a minimum in neritic waters to a maximum in SASW, whereas in summer-autumn a pCO_2 minimum developed mid-transect, which was associated with a nutrient minimum and the absence of core Southland Current water as a surface feature. This mid-transect minimum was observed on only 5 occasions from 1998 to 2005: in February 1998, November 1999, September 2000, January 2004 and September 2005. This feature, then, is not typical of summer/autumn as was hypothesised by Currie and Hunter (1998). In addition, the pCO_2 values reported for the years 1998 to 2005 in this paper are generally higher than those reported for 1992–1993 by Currie and Hunter (1998).

The dissolved reactive phosphate concentration data from January 1998 to December 2005 are shown in the form of a contour plot Fig. 3d. These data confirm the observations of Hawke (1989), that phosphate concentration increases with distance offshore. Concentrations vary from an observed minimum of 0.1 mmol m^{-3} occurring in inshore waters to a maximum of 1.1 mmol m^{-3} occurring in subantarctic surface waters in spring of most years. Nitrate concentrations (not shown) also increase with

distance offshore, the N:P ratio varies from less than 8 for inshore neritic waters, to 8–12 for the modified subtropical waters of the Southland Current, to 15–16 in subantarctic surface water. Samples for nutrient (phosphate and nitrate) analysis were taken less frequently from inshore waters (<20 km) from 2002 onwards. The sampling times are indicated by black dots in Fig. 3d.

For the purposes of this paper the remaining discussion will focus on data from subantarctic surface water, distances greater than 50 km along the transect. The variation of sea surface temperature and pCO_2 in SASW with time is shown in Fig. 4. The relevant data from each voyage have been averaged to give one point per voyage. The seasonal cycle in sea surface temperature (T_{sw}) is evident, the temperature varies from 8°C in winter to 12–13°C in summer. A simple sinusoidal harmonic fitted through this data (forced to a 365 day cycle, t=1 corresponds to January 1) is described by Eq. 2. This function has a mean value of 10.3°C and an amplitude of 2.1°C. The maximum temperature of 12.4°C occurs in mid-February (late austral summer), and the minimum of 8.2°C occurs in mid-August.

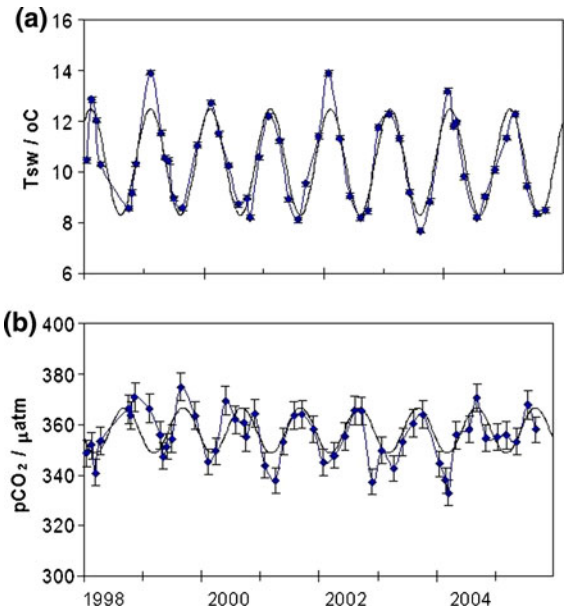

Fig. 4 Time variation of **a** sea surface temperature and **b** pCO_2 in SASW. The simple harmonic functions described by Eq. 2 and 3 are also shown

$$T_{sw} = 10.3 + 2.1 \sin\left(2\pi \frac{t - 317}{365}\right) \quad (2)$$

The annual cycle described by Eq. 2 explains 86% of the observed variance. Equation 2 is overlain on the measured T_{sw} in Fig. 4a. Including a linear trend with time gives a slope of -0.03 ± 0.04°C year^{-1}, however the fit is not improved.

The pCO_2 data also exhibit a seasonal cycle with a maximum in late winter/spring, and a minimum in late summer/autumn. 47% of the variation in pCO_2 data is explained by a harmonic cycle with a mean of 356 µatm, an amplitude of 9 µatm, and a maximum occurring in late August–early September (beginning of austral spring) (Eq. 3). Equation 3 is overlain on the measured pCO_2 in Fig. 4b.

$$pCO_2 = 356 + 9 \sin\left(2\pi \frac{t - 156}{365}\right) \quad (3)$$

Including a slope term in Eq. 3 gives a linear trend in pCO_2 with time of -0.4 ± 0.4 µatm year^{-1}, and this equation would explain 53 % of the variance. This decrease can almost be entirely explained by the linear temperature decrease.

A harmonic fit to the phosphate data (not shown) showed a phase very similar to the pCO_2 data suggesting that similar processes are affecting both parameters.

Discussion

The calculated carbon dioxide flux across the air-sea interface is determined from the concentration gradient across the interface, and a gas transfer velocity parameterised by wind speed. The daily air-sea flux was calculated from Eq. 4 (Liss 1983).

$$F = ks\Delta P \quad (4)$$

where k is the gas transfer velocity; s is the solubility of CO_2 in seawater at the in situ temperature and salinity, calculated using the algorithm of Weiss (1974); and ΔP is the CO_2 partial pressure difference across the air-sea boundary i.e. $\Delta P = pCO_2^{sw} - pCO_2^{air}$. The daily gas transfer velocity was calculated from the wind speed measured at Taiaroa Head (60 km from the study site, 76 m above sea level, K McGill, NIWA, personal communication and A

Sutherland, Port of Otago, pers comm) using the Wanninkhof (1992) relationship for short-term mean windspeed, and the Schmidt number determined from the in situ temperature and salinity. Taiaroa Head wind speed is recorded every 3 h, these data were averaged for the time interval cruise date ±1 week, the wind speed was not corrected to 10 m above the sea surface. Daily pCO_2^{sw} values were determined by simple linear interpolation of the bi-monthly measurements. The daily atmospheric pCO_2 was determined from the mole fraction of CO_2 measured at Baring Head (approx 650 km north of the transect site) during clean air conditions (A. Gomez, NIWA, personal communication), a standard atmospheric pressure of 1000 mbar, and water vapour pressure computed at the in-situ seawater temperature and salinity (interpolated measurements). The atmospheric carbon dioxide mole fraction measured at Baring Head was determined during southerly wind conditions only, therefore is representative of clean, background air. By convention, flux into the ocean is negative.

Two alternative parameterisations for the gas transfer velocity were also used in the flux calculations: that proposed by Liss and Merlivat (1986), and that proposed by Ho et al. (2006) (Table 1). The Liss Merlivat method gives values of k that are, on average, 1.6 times lower than the gas transfer velocities calculated using the Wanninkhof (1992) short term wind speed parameterisation. In addition we have used a more recent parameterisation of the gas exchange coefficient based on dual tracer experiments conducted close to our study site (Ho et al. 2006) and showing a quadratic dependence on wind speed. Values of k calculated this way are on average 1.16 times lower than those determined using the Wanninkhof (1992) method.

The wind speed data measured at Taiaroa Head is only a proxy for the wind speed at the location at which the pCO_2^{sw} was measured. The uncertainty that may arise from this assumption was investigated by comparing the flux determined using the Taiaroa Head wind speed averaged over the cruise-date ±1 week and the Wanninkhof (1992) short-term wind parameterisation for k, as described above, (termed "15-day Flux") with the flux calculated using wind speeds averaged over shorter and longer time periods. The flux determined using daily average wind speeds and the Wanninkhof (1992) short-term wind parameterisation for k gave annual fluxes on average 122% larger than the 15-day flux; that determined using annual average wind speeds (averaged over the calendar year) and the Wanninkhof (1992) long-term wind parameterisation for k gave annual fluxes on average 120% larger than the 15-day flux; and the flux determined using a single average wind speed determined over the 8 years of the study and the Wanninkhof (1992) long-term wind parameterisation for k gave annual fluxes on average 115% larger than the 15-day flux.

The daily net air-sea CO_2 flux, calculated as described above, is shown graphically in Fig. 5a. The flux varies from −10 to +3 mmol C m^{-2} day^{-1}, and is generally slightly more negative in summer/autumn and more positive in winter/spring. The daily air-sea flux values were combined to get an annual

Table 1 Integrated net annual air-sea CO_2 flux for SASW for the years 1998–2005, calculated using the wind speed parmaterisations of Wanninkhof (1992), Liss and Merlivat (1986), and Ho et al. (2006) for determining the gas transfer velocity (denoted W95, LM and H06 respectively)

Year	Flux (W92)/mmol C m^{-2} $year^{-1}$	Flux (LM)/mmol C m^{-2} $year^{-1}$	Flux (H06)/mmol C m^{-2} $year^{-1}$	Atmospheric source/sink
1998	1	0	1	Source
1999	82	53	71	Source
2000	−226	−148	−195	Sink
2001	−495	−318	−427	Sink
2002	−709	−457	−611	Sink
2003	−697	−380	−498	Sink
2004	−873	−563	−752	Sink
2005	−508	−332	−437	Sink
Takahashi et al. (2002)	−1,848			Sink
Takahashi et al. (2009)	−1,660			Sink

The flux from the Takahashi et al. (2002) and Takahashi et al. (2009) climatologies are also given

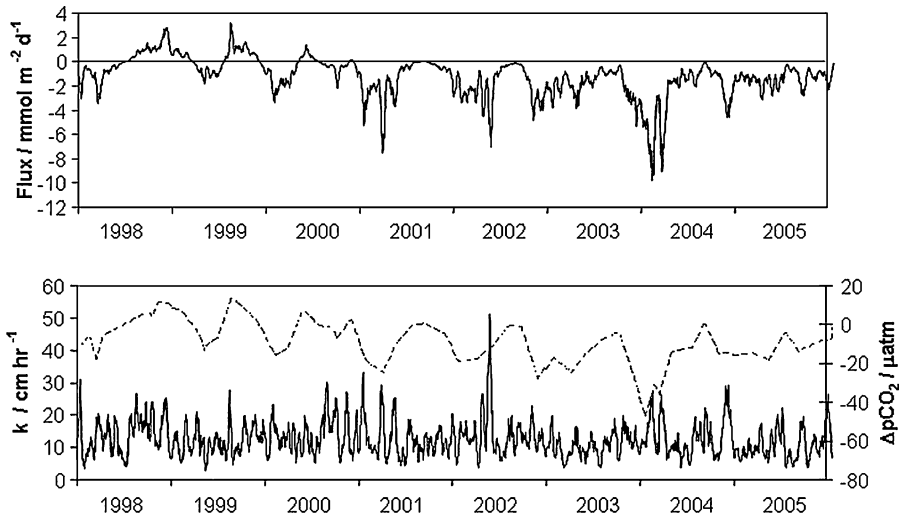

Fig. 5 **a** Time variation of air-sea CO_2 flux in SASW. **b** Time variation of the gas transfer velocity (k) using the Wanninkhof (1992) parameterisation (*solid line*, *left hand axis*) and ΔpCO2 (*dashed line*, *right hand axis*)

value for each year, the integrated annual values are given in Table 1. SASW acted as a sink for atmospheric carbon in all years except for 1998 and 1999, and the magnitude of the sink has been generally increasing with time.

Takahashi et al. (2009; and http://www.ldeo.columbia.edu/res/pi/CO2/carbondioxide/pages/air_sea_flux_2000.html) determined a flux of −1,660 mmol C m^{-2} $year^{-1}$ for the 4 × 5° grid box centered on 48°S, 172.58°E, the closest grid box to the study site. The Takahashi et al. (2009) climatology indicates a greater carbon sink than was observed during this study. The difference arises primarily from the difference in pCO_2^{sw} between this study and that of the climatology. The temperature and salinity data from this study are close to that of the Takahashi et al. (2009) climatology, however the mean pCO_2 in 2000 for this study was 358.1 µatm, as compared with the Takahashi et al. (2009) climatology value of 339.4 µatm.

The atmospheric carbon dioxide concentration is increasing with time primarily as a result of human activities. During the study period the concentration at Baring Head, Wellington, increased by 12.4 ppm from an annual average of 363.6 ppm in 1998 to 376.0 in 2005. The annual average wind speed at this site has been constant at 7.1 ± 0.3 ms^{-1} for the period 1998–2005 and therefore the value of the gas transfer velocity (k) has not varied (Fig. 5b). The magnitude of ΔpCO_2, however, has increased, from an annual average of −0.8 µatm in 1998, to +12.8 µatm in 2004 (Fig. 5b). The change in ΔpCO2 has been the main determinant of the increase in carbon flux into the ocean, and this in turn has increased primarily due to the increase in atmospheric CO_2 concentration.

There is no apparent long-term increase in surface pCO_2 measured at this subantarctic site. A simple analysis of the data indicates a temporal decrease in pCO_2 of (−) 0.4 ± 0.4 µatm $year^{-1}$, which can be explained by the observed decrease in water temperature of 0.03°C $year^{-1}$. A more rigorous analysis of the data is required to confirm this, and will be the subject of future work. Long term changes in pCO_2 (either directly measured or calculated from measurements of alkalinity and dissolved inorganic carbon concentration, C_T) have been observed at three other time series sites. At Station ALOHA (HOT) in the north Pacific Ocean an increase of 2.5 ± 0.1 µatm $year^{-1}$ (Keeling et al. 2004) has been deduced from the 14 year record, and attributed to the combined effects of uptake of anthropogenic carbon dioxide and changing freshwater input. An increase of 0.3 ± 0.3 µatm $year^{-1}$ has been reported in the north Atlantic Ocean, after analysis of the 20 year (1983–2003) combined Hydro S and BATS records (Bates and Keeling http://www.bios.edu/Labs/co2lab/research/IntDecVar_OCC.html). This rate of increase is similar to that expected from equilibration of those waters with anthropogenic CO_2 in the atmosphere. A pCO_2 increase of 1.55 ± 0.43 µatm $year^{-1}$ is reported for the ESTOC site in the North Atlantic Ocean (Santana-Casiano et al. 2007), and attributed to direct control of the total dissolved inorganic carbon

concentration due to increased atmospheric CO_2 concentration. It is not clear why an increase has not been observed at the Southern Ocean site reported here.

Conclusions

A time series transect has been established in the south-western Pacific Ocean, which includes subantarctic surface water. Data has been collected bi-monthly since 1998. The observed subantarctic pCO_2 data shows a seasonal cycle with a maximum in spring, and a minimum in autumn, with an amplitude of 10 µatm. The phase of the seasonal cycle is similar to that observed in the Indian Ocean SASW, although the amplitude at that site is much greater at 50 µatm (Metzl et al. 1999), than the 20 µatm observed in this study. The magnitude of the average air-sea CO_2 difference (ΔpCO_2) has increased over the 8 years from 1998 to 2005 as the atmospheric CO_2 concentration has increased while the annual average seawater pCO_2 has not apparently changed. This will have resulted in an increased flux into the surface waters. The annually integrated flux was small and positive in 1998 and 1999 i.e. the area was a source of atmospheric carbon dioxide, whereas since 2000 the area has been a sink. The annual flux determined for the study site is substantially less than that derived from the Takahashi et al. (2009) climatology.

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