pCO_2 IN SUBANTARCTIC SURFACE WATER: A TIME SERIES STUDY

K.I. Currie[1] and M.R. Reid[2]
[1]*National Institute of Water and Atmospheric Research Ltd (NIWA), PO Box 56, Dunedin, New Zealand; k.currie@niwa.co.nz*
[2] *Chemistry Department, University of Otago, PO Box 56, Dunedin, New Zealand; mreid@alkali.otago.ac.nz*

ABSTRACT
A time series transect has been established in subantarctic surface water off the south east coast of New Zealand. The 60 km long transect extends from the coast (45-46.20°S 170-43.20°E) to a station at 45-50.00°S 171-30.00°E. and sea surface temperature, salinity and pCO_2 have been measured bi-monthly since 1998 . SST, pCO_2 and pH of the subantarctic surface water show seasonal cycles that can be fitted with simple harmonic curves. Temperature has a mean value of 10.4°C, with an amplitude of 2.1°C, the maximum occurring in late summer. pCO_2 has a mean value of 360 μatm, an amplitude of 10 μatm, the maximum occurring in early spring. The phase of the pCO_2 and temperature curves are offset by 158 days, indicating that change in sea water temperature is not the major factor affecting pCO_2 in this area. The relative effects of temperature, biological utilization and air-sea gas exchange on the seasonal change in pCO_2 are determined using a simple model. The model results reproduce the timing of the observed pCO_2, however the amplitude of the changes is not well reproduced.

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 [*Murnane et al.*, 1999; *Takahashi et al.*, 1997; 2002; *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. The global flux map of *Takahashi et al.* [2002] shows a range of -5 to +1 moles CO_2 m^{-2} yr^{-1} uptake in the Southern Ocean and calculate the net sea-air flux of CO_2 in the Southern Ocean for the reference year 1995 to be -0.62×10^{15} gC yr^{-1}, accounting for 29% of the total global oceanic uptake. The distribution of carbon in high southern latitudes is generally not well modeled by global ocean carbon models, with disagreement on the location and magnitude of the Southern Ocean sink areas [*Sabine and Key*, 1998]. This is partly due to the incomplete understanding of the factors and processes controlling the carbonate chemistry in this region of the ocean. Subantarctic surface water (SASW) 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. In the southwest Pacific Ocean SASW is located to the south and east of the South Island of New Zealand.

A time series transect has been established from the coast of New Zealand to a station in SASW (45-50.00°S 171-30.00°E). Measurements of surface pCO2 plus supporting data (temperature, salinity, nutrient concentration) have been made bi-monthly since 1998. pH of the surface water has been measured since 2002.

The sea surface temperature (Tsw) and pCO2 of the SASW can be described by simple harmonic equations:

$$Tsw = 10.4 + 2.1 \sin\left(2\pi \frac{t-318}{365}\right)$$

$$pCO_2 = 360 + 10 \sin\left(2\pi \frac{t-160}{365}\right)$$

Temporal changes in pCO_2 can, in theory, be separated into the processes which contribute to the variation, as represented by the following equation [*Poisson, Metzl* et al. 1993].

$$\frac{\Delta P}{\Delta t} = [\frac{\delta P}{\delta t}]_T + [\frac{\delta P}{\delta t}]_F + [\frac{\delta P}{\delta t}]_B + [\frac{\delta P}{\delta t}]_H + [\frac{\delta P}{\delta T}]_V$$

where P is pCO_2, t is time and the subscript T refers to the effect of changing temperature on pCO_2 (thermodynamic effect), B is the effect of net biological uptake of CO_2 (biological effect), F is the effect of air-sea exchange, H and V are the effects of horizontal and vertical mixing respectively. This deconvolution model was applied to the SASW: the temperature effect was determined using the temperature change algorithms of *Copin-Montegut* [1988; 1989]; the biological effect was estimated using the change in phosphate concentration as a proxy for change in total carbon concentration due to biological activity; and the air-sea flux was calculated from the air-sea pCO_2 difference and a gas exchange constant using the *Wanninkhof* [1992] short-term wind speed parameterization. The contributions of vertical and horizontal mixing are unable to be assessed from the available data.

Deconvolution of the temporal changes in pCO_2 indicates that the temperature effect is offset by the biological effect, and that the sum of the effects of temperature, biology and air-sea exchange can explain the timing of the pCO_2 signal, although the modeled values are in general about 10 μatm less than the observed values.

REFERENCES

Copin-Montegut, C., A new formula for the effect of temperature on the partial pressure of CO_2 in seawater., *Marine Chemistry*, *25*, 29-37, 1988.

Copin-Montegut, C., A new formula for the effect of temperature on the partial pressure of CO_2 in seawater. Corrigendum., *Marine Chemistry*, *27*, 143-144, 1989.

Murnane, R.J., J.L. Sarmiento, and C. Le Quere, Spatial distribution of air-sea CO_2 fluxes and the interhemispheric transport of carbon by the oceans, *Global Biogeochemical Cycles*, *13* (2), 287-305, 1999.

Sabine, C.L., and R.M. Key, Controls on fCO_2 in the South Pacific, *Marine Chemistry*, *60*, 95-110, 1998.

Takahashi, T., R.A. Feely, R.F. Weiss, R.H. Wanninkhof, D.W. Chipman, S.C. Sutherland, and T.T. Takahashi, Global air-sea flux of CO_2: An estimate based on measurements of sea-air pCO_2 difference, *Proceedings of the National Academy of Sciences, USA*, *94*, 8292-8299, 1997.

Takahashi, T., S.C. Sutherland, C. Sweeney, A. Poisson, N. Metzl, B. Tilbrook, N. Bates, R. Wanninkhof, R.A. Feely, C. Sabine, J. Olafsson, and Y. Nojiri, Global sea-air CO_2 flux based on climatological surface ocean pCO_2, and seasonal biological and temperature effects, *Deep-Sea Research II*, *49*, 1601-1622, 2002.

Tans, P.P., I.F. Fung, and T. Takahashi, Observational constraints on the global atmospheric CO_2 budget, *Science*, *247*, 1431-1438, 1990.

Wanninkhof, R., Relationship between wind speed and gas exchange over the ocean, *Journal of Geophysical Research*, *97* (C5), 7373-7382, 1992.