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TELLUS

Atmospheric CO_2 concentrations and $\delta^{13}C$ values across the Antarctic Circumpolar Current between New Zealand and Antarctica

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ABSTRACT

Measurements of atmospheric CO_2 concentrations were repeatedly carried out on the vessel 'Italica' of the Italian National Research Program in Antarctica, during cruises from Italy to Antarctica. Discrete air samples were also collected in 4-L Pyrex flasks during these cruises in order to carry out $\delta^{13}C$ analyses on atmospheric CO_2. The results acquired between New Zealand and Antarctica are reported here. The mean growth rate of the CO_2 concentration from 1996 to 2003 in this area of the Southern Oceans is of about 1.8 ppmv yr^{-1}, in good agreement with NOAA/CMDL measurements. The rates of increase from cruise to cruise are rather variable. From 1996–1997 to 1998–1999 cruise the yearly growth rate is 2.75 ppmv yr^{-1}, close to the large growth rates measured in several areas and mainly related to the most severe El Niño event of the last years. The other yearly growth rates are of about 1.3 and 2 ppmv for the periods 1998–1999 to 2001–2002 and 2001–2002 to 2003–2004, respectively. The large difference between these two values is probably related to the uncertainty on the only two 2001–2002 discrete measurements of CO_2 concentration in this area. The measured $\delta^{13}C$ values show two completely different distributions and a large interannual variability. The 1998–1999, 2002–2003, and 2003–2004 results obtained between about 55°S and 65°S across the Antarctic Polar Front show a marked negativization of up to more than 2‰ when compared to the background values. The results are related to local source regions of CO_2, as frequently found in the Southern Ocean by several authors; the negative $\delta^{13}C$ values are tentatively related to the possible contribution of different causes. Among them, the southward negative gradient of $\delta^{13}C$ of the dissolved inorganic carbon, the contribution from upwelling deep waters and from subsurface processes between the Northern SubAntarctic Front and the Polar Front, and, partly, the contribution of CO_2 of biogenic origin, e.g. from heterotrophic activity. The 2001–2002 results are very homogeneous and almost constant, close to −8.5‰, showing only minor deviations from the oceanic background values. This behaviour may be related to differences in the frontal structure along the 2001–2002 track.

1. Introduction

Despite the massive production of CO_2 by anthropogenic activities, its growth rate in the atmosphere is considerably lower than expected. According to recent estimates (Houghton et al., 2001; Sarmiento and Gruber, 2002) during the last 20 yr the atmospheric growth rate was about 50% of the anthropogenic production. The remaining CO_2 was taken up by the ocean and the land biosphere (IPCC, 2001). Unfortunately, increasing deforestation and warming of ocean water will decrease the future uptake of CO_2. Predictions of future atmospheric loading of CO_2 and its consequences for the global climate can be supported only by a precise understanding of the natural sinks and sources of carbon dioxide, this gas being one of the primary agents of global climate changes (e.g. Conway et al., 1994; Kattenberg et al., 1995). During the last fifteen years several authors found that Southern Oceans as well as the Circumpolar Current can behave as a sink but also as a source of CO_2 depending on different environmental conditions. The Antarctic as well as the sub-Antarctic zone, considered a strong oceanic sink of atmospheric CO_2 (e.g. Siegenthaler and Sarmiento, 1993; Metzl et al., 1995, Caldeira and Duffy, 2000) showed a high temporal and space variability of the regional air–sea CO_2 fluxes, biological as well as physical processes driving the oscillations of the air–sea CO_2

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fluxes. The data by Takahashi et al. (1993, 1997) '*suggested that a temperature component is largely responsible for the observed distribution of surface water partial pressure of* CO_2' (Stoll et al., 2002). Papers by Bakker et al. (1997), Hoppema et al. (1995, 1999) and Metzl et al. (1999) showed that plankton blooms are even more important than temperature, the summer values and distribution of the fCO_2 being frequently under biological control. Light and iron probably regulate these blooms according to De Baar and Boyd (2000). Takahashi et al. (2002) '*separated the biological component in seasonal* pCO_2 *changes from the temperature change component*' showing that '*biological processes strongly control the subpolar-polar oceans and the coastal waters around Antarctica including the Ross Sea*'. Poisson et al. (1993) and Hoppema et al. (2000) pointed out the presence of frequent and large oscillations of the air–sea flux of CO_2 in the Antarctic and sub-Antarctic regions of the Indian Ocean and in the Weddell Sea, respectively. Stoll et al. (2002) pointed out the presence of oscillations of the air–sea flux of CO_2 in the Weddell Sea between the Polar Front and the Antarctic Continent, the air–sea fluxes ranging from -9 to $+7$ mmol m^{-2} d^{-1} '*making these regions act as a sink as well as a source of* CO_2'. At about 50°S these authors found a large supersaturation in fCO_2 relative to the atmosphere, of up to 75 μatm.

Despite all the studies carried out in the Antarctic and sub-Antarctic zone, direct measurements of the atmospheric CO_2 concentrations and of its carbon isotope values have never been carried out in that area with the only exception of three carbon isotope measurements obtained by Inoue and Sugimura (1986) from composite air samples. We report here the CO_2 concentrations measured during different cruises between Italy and Antarctica (Mediterranean, Red Sea, Indian Ocean, Southern Ocean to Littleton, N.Z., Antarctica, Terra Nova Bay) and the carbon isotope composition of atmospheric CO_2 from discrete air samples collected along the New Zealand to Antarctica route on four different cruises. The carbon isotope values of CO_2 from discrete air samples collected between Italy and New Zealand were reported and discussed in a previous paper (Longinelli et al., 2005). All the results obtained will soon be made available in a public database (CDIAC).

2. Analytical techniques

Records of the CO_2 concentrations in the ocean atmosphere between Italy and Antarctica were made, over the last decade, on a vessel of the Italian National Research Program in Antarctica by means of a Siemens Ultramat 5E analyser assembled for shipboard use (Ori et al., 1996; Lenaz et al., 2000; Longinelli et al., 2001; Longinelli et al., 2005). Its measurement system is based on the comparison between two signals from two infrared absorbing cells, one filled with a flux of synthetic air with constant CO_2 concentration and the other filled with the air sample carefully dried by means of a cold trap ($t < -50°C$). During the 2001–2002 cruise, technical problems prevented the recording of continuous measurements so that only a few discrete measurements could be carried out on that journey. During the 2002–2003 cruise we were allowed to collect only flask samples between New Zealand and Antarctica. During the 2003–2004 cruise, further minor instrumental problems prevented the collection of a continuous record in the Central Indian Ocean between the equator and 40°S.

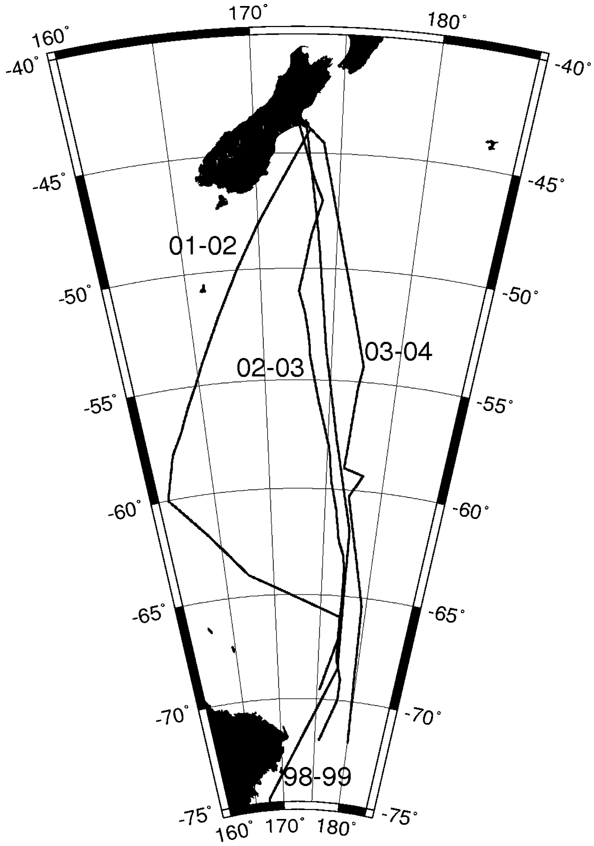

Fig. 1. New Zealand to Antarctica routes of the M/V *Italica* along which flask air samples have been collected and atmospheric CO_2 concentrations measured. The latter measurements could not be carried out during the 2002–2003 cruise.

On the last four cruises (1998–1999; 2001–2002; 2002–2003; 2003–2004; Fig. 1), discrete air samples were collected by means of 4-L Pyrex flasks in order to have a record of the carbon isotopic composition of atmospheric CO_2 through time and space. For the collection of the air samples the 4-L Pyrex flasks were evacuated to better than 5×10^{-3} mmHg (the vacuum that can be obtained on board the ship by means of a two stage rotary pump) and then opened on the windward side of the ship, about 15 m above sea level. After the sample collection, the flasks were closed by means of greaseless high vacuum stopcocks and stored in wooden boxes until the ship's arrival at its final harbour in Italy, about 3–4 months later. The quantitative separation of the CO_2 from air was obtained in the laboratory by pumping the flask air samples in a high vacuum line at a rate of about 7–8 mL/min.

through a Swagelock microvalve and a spiral Pyrex trap cooled in liquid nitrogen. After the completion of the air pumping, the Pyrex trap was isolated by means of high vacuum stopcocks and heated to about −80°C by means of an ethyl alcohol-liquid nitrogen slash. The evolved CO_2 was then collected in a sample tube and measured in a Finnigan Delta S mass spectrometer. All the isotopic values are reported here in terms of δ units (permil deviation of the isotope ratio from that of the international standard used). δ is defined by the relationship: $\delta = [(R_{\mathrm{sample}} - R_{\mathrm{stand.}})/R_{\mathrm{stand.}}] \times 10^3$ where $R = {}^{18}O/{}^{16}O$ or ${}^{13}C/{}^{12}C$. The laboratory standard CO_2 used for these measurements was prepared twice a week from a very pure Carrara marble whose isotopic composition is −2.43 ($\delta^{18}O$) and +2.45 ($\delta^{13}C$), calibrated versus NBS-19 and NBS-20. The values used for this calibration are: NBS-19, −2.20 ($\delta^{18}O$) and +1.95 ($\delta^{13}C$); NBS-20, −4.14 ($\delta^{18}O$) and −1.06 ($\delta^{13}C$). These NBS standards, in turn, were directly calibrated versus the original PDB-1. We think that this justifies the use of PDB-1 as a reference standard throughout this paper. The accuracy of this procedure has been repeatedly tested on several air samples collected simultaneously, with the same technique, and treated in the same way. The standard deviation of the carbon isotope measurements determined on these samples was $\pm 0.03 \pm 0.01‰$ (1σ). The standard deviation of the results obtained from all the air samples from the Southern Ocean should be equal or, at least, very close to this value. The raw isotopic results obtained from flask air samples have been corrected for the N_2O contribution according to the equation reported by Mook and van der Hoek (1983). As reported by Longinelli et al. (2005) the theoretical correction for the presence of N_2O is $+0.1779 \pm 0.003$. The value used is +0.18‰.

3. Results and discussion

The overall distribution of the values obtained by measuring the atmospheric CO_2 concentration from Italy to Antarctica during four cruises is reported graphically in Fig. 2. These measurements allow the calculation of the mean growth rate of the CO_2 from December 1996 (no flask samples were collected during that cruise) to January 2004 as well as the CO_2 increase from period/cruise to period/cruise. The former value, calculated from the data obtained between New Zealand and Antarctica, is of about 1.8 ppmv yr^{-1}, in very good agreement with the NOAA/CMDL CO_2 measurements carried out e.g. at the Cape Grim site, Tasmania (White and Tans, 2005). The growth rates from period/cruise to period/cruise, again calculated from the Southern Ocean data, are quite variable. From the 1996–1997 to the 1998–1999 cruise the CO_2 concentrations increased by about 5.5 ppmv with an yearly rate of 2.75 ppmv yr^{-1}, not far from the large growth rates measured for the period 1997–1998 in other areas, for example, Cape Grim, Tasmania in the southern hemisphere (Tans, 2000) and Monte Cimone, Italy in the northern hemisphere (Colombo et al., 2000). These large growth rates were obviously related to the anthropogenic activity but also to a significant contribution from the most severe and persistent El Niño event of the last years. The CO_2 growth rates evaluated for the 1998–1999 to 2001–2002 and 2001–2002 to 2003–2004 time intervals are considerably lower (about 1.3 and 2 ppmv yr^{-1}, respectively) and not too far from the overall growth rate for the whole time interval. The relatively large difference between these two values may be, at least partially, related to the large uncertainty on the only two discrete measurements carried out in this area during the 2001–2002 cruise, because of the major technical problems experienced during that cruise. The isotopic results obtained from the first set of flask samples collected during the 1998–1999 cruise were published elsewhere, along with the results of continuous measurement of the atmospheric CO_2 concentration (Longinelli et al., 2001). The samples collected between New Zealand and Antarctica during that cruise showed, at the latitude of about 58°S a couple of isotopically anomalous data, considerably lighter than expected if we consider the

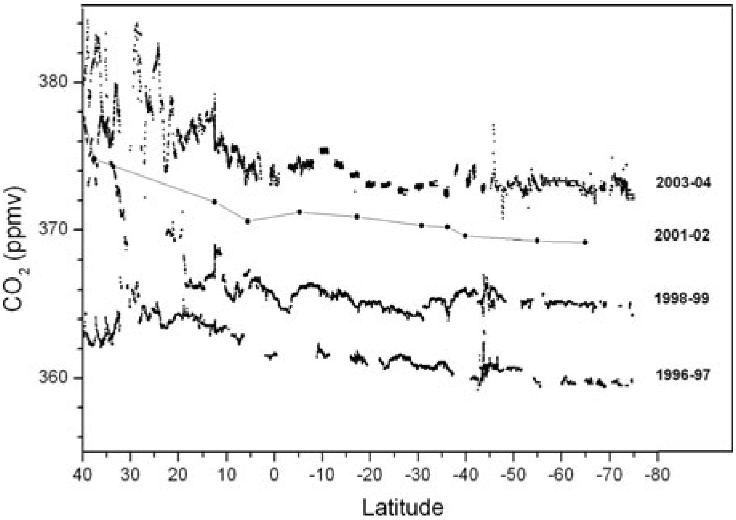

Fig. 2. Atmospheric CO_2 concentrations (ppmv) measured along the route between Italy and Antarctica during the reported four cruises. Only a few discrete measurements were carried out during the 2001–2002 expedition because of technical problems to the Siemens Analyser. Flask samples were not collected during the 1996–1997 cruise.

distance from continental areas and the extremely improbable contribution of pollution from the continent. During the following cruises the number of samples collected between New Zealand and Antarctica was increased as much as possible, due to the importance of carbon isotope measurements in that area and the shortage of these data from Southern Ocean. Unfortunately, the measurement of several other variables that would be very important for this study, such as the CO_2 partial pressure in surface water (pCO_2), CO_2 fugacity (fCO_2), etc. was always prevented by a number of problems among which the specific restrictions imposed by the Antarctic Project management. Despite these limitations, the measurement of CO_2 concentrations and of the carbon isotope composition of the CO_2 from flask air samples were carried out with the hope that some further light could be shed on the air–sea fluxes in that section of the Southern Ocean. All the samples from the four cruises (1998–1999, 2001–2002, 2002–2003, 2003–2004) were collected during the same period of the year, between about December 25 and January 5, along New Zealand to Antarctica routes quite similar to one another (Fig. 1). The isotopic results obtained are reported graphically in Fig. 3. It must be pointed out that, during these cruises, no major changes of the atmospheric CO_2 concentrations were observed as being directly related to the measured changes of the $\delta^{13}C$ values. Taking into account that the Siemens Ultramat 5E analyzer integrates every 10 min the values measured every two seconds, small variabilities like those recorded during the 2003–2004 cruise, may reflect considerably larger transient changes of the measured variable. The most interesting aspects of the $\delta^{13}C$ results are: the rather large variability exhibited by several samples, the increasing frequency through time of the isotopically light values despite the unlikelihood of contamination by anthropogenic activities, and the concentration of the lightest values in the latitudinal belt between about 55°S and 65°S. The possibility of a repeated contamination from the ship exhaust must be ruled out for several reasons and, first of all, because on a sailing ship it is practically impossible to contaminate samples collected windward. The measured $\delta^{13}C$ values show two different distributions: the samples collected during the 2001–2002 cruise yielded $\delta^{13}C$ values fairly close to one another and not far from about −8.5‰. This value is slightly more negative (about −0.4‰) than the mean 1998 background value (−8.1‰) (Fig. 3). No markedly anomalous $\delta^{13}C$ have been obtained from these samples at the latitudes 55°S–65°S. One should conclude that only minor changes in the regional background atmospheric CO_2 took place, the overall conditions being not far from those existing at lower latitudes. These minor changes may be tentatively related to the moderate southward decline of the $\delta^{13}C_{DIC}$ measured in various areas of the Southern Ocean. Archambeau et al. (1998) measured a maximum decline of about −1‰ along a section from South Africa to Antarctica (70°S) at 30°E; Gruber et al. (1999) measured an overall gradient of about −0.5‰ from about 43°S to about 60°S in the Central Southern Pacific; McNeil et al. (2001) during two different cruises south of Australia measured a southern gradient of −0.4 ‰ between 52°S and 60°S and a gradient of −0.9 ‰ between 52°S and 65°S. The isotopic shift of our 2001–2002 measurements is compatible with the reported isotopic shifts of $\delta^{13}C_{DIC}$ in Southern Oceans. However, it should be pointed out that the ship track in 2001–2002 was different than all other tracks (Fig. 1). According to the satellite images of the SST distribution in January in this area (Web page: iridl.ldeo.columbia.edu/etc. and Moore et al., 1999) the frontal structure appears to be rather different at about 160°E and 175°E with a marked southward shift in the latter region and this could justify the difference between our 2001–2002 results and all the other results obtained at the same latitude but different longitude. The spatial and temporal variability of the Polar Front in this region is explained (Moore et al., 1999) by the vorticity constrains on the dynamics of the Polar Front caused by the topography features of the Southern Ocean. The samples from 1998 to 1999, 2002 to 2003 and 2003 to 2004 cruises behave in a completely different way showing, particularly between about 55° and 65°S, isotopic values rather variable but considerably lighter than the background values measured during the 1998–1999 cruise. Despite a number of studies on Southern Ocean, the only $\delta^{13}C$ values of atmospheric CO_2 reported by previous author in the studied area are those by Inoue and Sugimura (1986). Three measurements were carried out by these authors on composite air samples collected presumably between December 1983 and January 1984 between 40°S and 50°S ($\delta^{13}C = -8.08$), between 50°S and 60°S ($\delta^{13}C = -7.98$) and at about 60°S ($\delta^{13}C = -7.88$). The average value of pCO_2 reported for the same sections was almost constant at about 341.6 ± 1.0 ppm (the authors use ppm throughout the paper to report the CO_2 concentration). These three $\delta^{13}C$ values are rather negative for that period. Extrapolating the results reported by the NOAA stations in that area (Cape Grim, Tasmania, and South Pole) the $\delta^{13}C$ of atmospheric CO_2 at that time should have been of about −7.5‰. If we correct the values reported by Inoue and Sugimura (1986) for the probable effect of the N_2O (+0.23‰

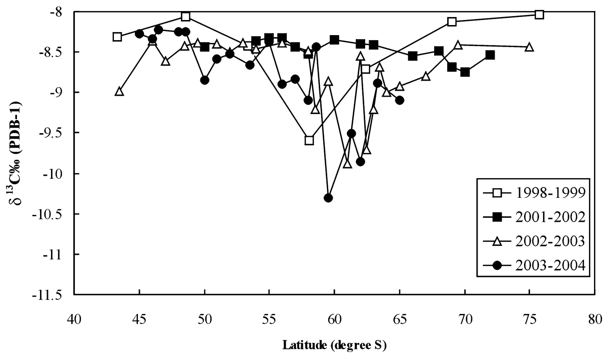

Fig. 3. $\delta^{13}C$ values of CO_2 from discrete air samples collected between New Zealand and Antarctica during four cruises. All the samples were collected in the last days of December and/or the very first days of January.

according to the mass spectrometer characteristics reported by the authors), the three δ^{13}C values are still more negative than expected by about −0.4 to −0.2‰. As in the case of our 2001–2002 samples, this small difference could be related to a southward decline of the $\delta^{13}C_{DIC}$. However, a quantitative comparison with our results is rather difficult because of the laps of time (about 15–20 yr) and the shift of both the atmospheric CO_2 concentration and the background δ^{13}C in that area. The number of isotopically anomalous values reported in Fig. 3 and their shift from the background value measured in oceanic areas suggest, for this period of austral summer, the possibility of rather frequent contributions to the atmosphere of isotopically light CO_2, particularly from surface waters of a latitudinal belt of about 10° in width across the Polar Front, without sensible shift from air–sea equilibrium conditions. All the estimates of the oceanic CO_2 fluxes based on the observed $\Delta p CO_2$ values between surface ocean and atmosphere suggested large Southern Ocean uptakes during austral summer. Recent atmospheric inversion estimates (Gurney et al., 2003; Roy et al., 2003) showed that, south of 50°S the Southern Ocean behaves as a summer sink even though the calculated uptakes are considerably smaller than those previously estimated. However, these conclusions are reliable at a large scale but not necessarily at a mesoscale and smallscale. In fact, several authors measured contrasting source/sink distributions at a mesoscale and smallscale in other sectors of the Southern Ocean. Several in situ measurements of surface pCO_2 revealed mostly undersaturation conditions (e.g. Murphy et al., 1991; Poisson et al., 1994; Hoppema et al., 1995; Robertson and Watson, 1995; Bakker et al., 1997; Hoppema et al., 2000) but local source areas have been repeatedly detected as well (Poisson et al., 1993; Hoppema et al., 2000; Stoll et al., 2002) confirming the very high spatio-temporal variability of surface pCO_2 suggested by Poisson et al. (1993). The latter authors, during their 1991 campaign in the Antarctic and Subantarctic areas of the Indian Ocean found, between about 46° and 64°S (between about 63° and 83°E) '*a mosaic of CO_2 sink, source and near-equilibrium zones*'. They observed seasonal, monthly and even daily variations of fCO_2: gradients of up to 40 μatm/10 km were observed '*linked to a well-marked hydrological front*' as well as fCO_2 decrease of 10 μatm in 10 hr, biological activity being probably responsible for such a decrease. Hoppema et al. (2000), confirming a large spatial and short-term temporal variability in the Southern Ocean calculated, for early autumn, outfluxes of up to 5.47 mmol m^{-2} d^{-1} in the Eastern Weddell Sea for an area between 52° and 56°S while, within the northern Weddell Gyre both sources and sinks were found, approximately equal in magnitude. Stoll et al. (2002) carried out a two month cruise (December 1995–January 1996) in the Weddell Sea from about 50°S to 70°S measuring the fCO_2 in air and seawater along with a number of other variables among which sea water temperature, salinity, Chlorophyll *a* and nutrient concentration. These authors found that undersaturation or supersaturation values may increase or decrease in a matter of days, the net production varying in some areas between −9 and +7 mmol m^{-2} d^{-1}. These changes have been related to various causes among which large oscillations in the dominance of autothrophic (CO_2 fixation) versus heterothrophic (CO_2 respiration) activity, upwelling of deep waters rich in dissolved CO_2, and mixing of different waters. It is of importance the Stoll et al. (2002) observation that often no clear correlation can be seen between Chlorophyll *a* levels and CO_2 concentration in the water. This is because high Chlorophyll *a* abundance does not necessarily mean a large undersaturation of CO_2 in the wind mixed layer, because different groups of phytoplankton may be present. Along with diatoms, dinoflagellates, primnesiophytes and chrysophytes may be present, their behaviour, as regards CO_2 uptake, being not homogeneous. Finally, it should be pointed out that biological processes, with their high propensity for patchiness, may cause large variations of the superficial conditions, mainly in summer (Hoppema et al., 2000; Stoll et al., 2002). These observations refer to areas of the Southern Ocean far from those which our samples come from. However, there is no reason to believe that the Southern Ocean between New Zealand and Antarctica behaves in a drastically different way. An important remark is that while instantaneous measurements of most of the important variables are quite valid to represent local environmental conditions, the extrapolation of these data in space and more notably in time over periods of weeks, months or years is not advisable because of the large spatial and short-temporal variability that may affect these variables. Accordingly, if we compare our δ^{13}C data with other variables measured weeks, months or years away, the conclusions that can be drawn may be debatable and, in some case, even misleading. Because of the lack of precise measurements of other variables carried out simultaneously with the collection of our samples and according to the above considerations we think that the following main points should be considered to validate our results:

(1) The measured δ^{13}C values involve local conditions of CO_2 supersaturation of surface ocean water making some areas act as a source of CO_2. The data reported by previous papers show that this assumption is reasonable, the discontinuity of the isotopic results within the 55°–65°S latitudinal belt being in favour of a considerable variability of air–sea fluxes at mesoscale and smallscale, as repeatedly observed in other Southern Ocean sections.

(2) The CO_2 escaping from the ocean surface should have, in this case, δ^{13}C values sufficiently low to help decrease the carbon isotope composition of atmospheric CO_2 to values considerably lower than background values. Because of the lack of direct measurements of variables which may help to suggest the origin of these values, we can only consider the different causes which may contribute to produce these data.

As reported by several authors (Archambeau et al., 1998; Gruber et al., 1999; McNeil et al., 2001) meridional profiles of $\delta^{13}C_{DIC}$ show southern negative gradients ranging from about −0.4 to about −1‰. The reported shifts are insufficient to fully explain our results, however a partial contribution of these southern gradients can be reasonably considered.

Upwelling of deep waters, rich in dissolved CO$_2$ with low δ^{13}C resulting from remineralization of organic matter, normally occur at slightly higher latitudes (e.g. Craig et al., 1981; Russo et al., 1999). The upwelled water may be transported northward by Ekman transport and its low δ^{13}C imprint may be at least partially saved after mixing with Antarctic Surface water and contribute to the measured atmospheric values.

The fCO$_2$ distribution in the surface layer may be at least partially dependent on subsurface processes as well. In the same area between New Zealand and Antarctica, Russo et al. (1999) found, between the beginning of January and mid February 1996, a triple cold core feature located between the Northern Sub Antarctic Front (about 52°S) and the Southern Sub Antarctic Front (about 58°S) at depths of about 60 m; a weaker signature of their presence could be observed also in the surface layer. Several other minor cold features were observed between the SSAF and the Polar Front (62°/63°S). These eddies or meanders were observed almost at the same position throughout the reported period, incorporating nuclea of Antarctic Surface Water. These features could also contribute to a CO$_2$ supersaturation of surface water with isotopically low values of the dissolved CO$_2$. The possibility of a CO$_2$ increase in the surface layer due to the influx of CO$_2$ related to eddy-diffusive influx from underlying water layers was discussed also by Stoll et al. (2002).

A further interesting point refers to the consideration by the latter authors on the possible relationships between Chlorophyll *a* and CO$_2$ concentration. Uptake conditions or outgassing conditions within the wind mixed layer may be related to the dominance of autotrophic versus heterotrophic activity or vice versa.

Finally, remineralization processes of decomposing planktonic organic matter [very high concentrations of dissolved oxygen can be found in this area (Craig et al., 1981)] may help to produce CO$_2$ with extremely low ^{13}C/^{12}C ratios (Lourey et al., 2004).

The above considerations suggest a reasonable interpretation of the observed anomalous δ^{13}C values but seem in contrast with the isotopic results obtained at latitudes higher that 62°/63°S. Surface waters south of this latitude should be interested '*a fortiori*' by high concentrations of CO$_2$ with low δ^{13}C values, because of the large contribution of isotopically light CO$_2$ supplied by the upwelling water masses. On the contrary, the δ^{13}C of atmospheric CO$_2$ at latitudes equal to or higher than about 65°S tend to less negative values, only slightly lower than the background values measured over the oceans (Longinelli et al., 2005). This behaviour could be related to the southern distribution of surface water temperatures that, south of the Polar Front, are generally close to zero or even below zero (Craig et al., 1981; Rintoul et al., 1997; Russo et al., 1999). These extreme environmental conditions may prevent, or at least drastically reduce, positive air–sea fluxes because of the CO$_2$ solubility at low temperature.

4. Summary and conclusions

Repeated measurements of atmospheric CO$_2$ concentrations carried out through time between New Zealand and Antarctica, showed concentrations and yearly growth rates quite close to those measured at land-based NOAA/CMDL stations in that area. Discrete air samples collected during austral summer between New Zealand and about 75°S showed several δ^{13}C values of atmospheric CO$_2$ considerably lighter than the background values measured over the oceans. These values are related to a mosaic, at small scale, of positive air–sea fluxes. Similar source areas have been repeatedly observed by various authors in other sections of the Southern Ocean. The markedly negative δ^{13}C values of CO$_2$ escaping from the ocean surface can be tentatively related to partial contributions by different causes such as the southern negative gradient of $\delta^{13}C_{DIC}$, the upwelling of deep waters and their northward transport, subsurface mixing processes and, finally, the possible contribution of biological heterotrophic activity and the production of isotopically light CO$_2$ by remineralization processes of decomposing planktonic organic matter.

5. Acknowledgments

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