

# Air-Sea CO<sub>2</sub> fluxes in the Atlantic as measured during boreal spring and autumn

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Received: 18 May 2009 – Published in Biogeosciences Discuss.: 12 June 2009 Revised: 21 April 2010 – Accepted: 23 April 2010 – Published: 18 May 2010

Abstract. A total of fourteen hydrographic cruises from 2000 to 2008 were conducted during the spring and autumn seasons between Spain and the Southern Ocean under the framework of the Spanish research project FICARAM. The underway measurements were processed and analysed to describe the meridional air-sea  $CO_2$  fluxes ( $FCO_2$ ) in the covered sector of the Atlantic Ocean. The data has been grouped into different biogeochemical oceanographic provinces based on thermohaline characteristics. The spatial and temporal distributions of  $FCO_2$  followed expected distributions and annual trends reproducing the recent climatological  $\Delta f CO_2$  estimations with a mean difference of  $-3 \pm 18 \,\mu$ atm (Takahashi et al., 2009). The reduction in the CO<sub>2</sub> saturation along the meridional FICARAM cruises represented an increase of  $0.02 \pm 0.14 \text{ mol m}^{-2} \text{ yr}^{-1}$  in the ocean uptake of atmospheric CO<sub>2</sub>. The subtropical waters in both Hemispheres acted as a sink of atmospheric CO<sub>2</sub> during the successive spring seasons and as a source in autumn. The coarse reduction of the ocean uptake of atmospheric CO<sub>2</sub> observed in the North Atlantic Ocean was linked to conditions of negative phase of the North Atlantic Oscillation that prevailed during the FICARAM period. Surface waters in the North Equatorial Counter Current revealed a significant longterm decrease of sea surface salinity of  $-0.16 \pm 0.01 \,\mathrm{yr}^{-1}$ coinciding with a declination of  $-3.5 \pm 0.9 \,\mu \text{atm yr}^{-1}$  in the air-sea disequilibrium of CO2 fugacity and a rise of oceanic CO<sub>2</sub> uptake of  $-0.09 \pm 0.03 \text{ mol m}^{-2} \text{ yr}^{-1}$ . The largest CO<sub>2</sub> source was located in the equatorial upwelling system. These tropical waters that reached emissions of  $0.7 \pm 0.5$  and  $1.0 \pm 0.7 \,\mathrm{mol}\,\mathrm{m}^{-2}\,\mathrm{y}^{-1}$  in spring and autumn, respectively,



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showed an interannual warming of  $0.11 \pm 0.03$  °C yr<sup>-1</sup> and a wind speed decrease of  $-0.58 \pm 0.14$  m s<sup>-1</sup> yr<sup>-1</sup> in spring cruises which suggest the weakening of upwelling events associated with warm El Niño – Southern Oscillation episodes. Contrary the surface waters of the Patagonian Sea behaved as an intense sink of CO<sub>2</sub> in March and November. The oceanic waters of the convergence of Falkland and Brazil Currents showed the strongest CO<sub>2</sub> absorption with a rate of  $-5.4 \pm 3.6$  mol m<sup>-2</sup> yr<sup>-1</sup> in November. The Southern Oceans sampled in the Drake Passage behave as an average uptake rate of  $-1.1 \pm 0.9$  mol m<sup>-2</sup> yr<sup>-1</sup> while the distal shelf of the Livingston Island acted as a slight source of CO<sub>2</sub> to the atmosphere.

### 1 Introduction

The CO<sub>2</sub> emissions associated with human activity, such as fossil fuel burning, changes in land-use or cement production, have increased atmospheric CO<sub>2</sub> concentrations (Keeling and Whorf, 2000; Houghton, 2003) from preindustrial levels (~270 ppm; parts per million of volume) to present-day ones, above 384 ppm (Solomon et al., 2007). Despite current total CO<sub>2</sub> emissions to the atmosphere of ~9.1 PgC yr<sup>-1</sup> (Canadell et al., 2007) only half of them are retained in the atmospheric reservoir (Sarmiento and Gruber, 2002; Sabine et al., 2004). Oceanic and terrestrial ecosystems sequestrate important amounts of CO<sub>2</sub>, thus reducing atmospheric CO<sub>2</sub> accumulation. The combined storage of land and oceans mitigates significantly the rate of global warming by quenching the global temperatures sensed in the biosphere (Siegenthaler and Sarmiento, 1993).

Cruise	Ship	Date	Latitude range
FICARAM 1	R/V Hespérides	Oct-Nov, 2000	36.5° N–11.1° S
FICARAM 2	R/V Hespérides	Mar–Apr, 2001	40° N-55.1° S
FICARAM 3	R/V Hespérides	Oct-Nov, 2001	36.6° N-7.8° S
FICARAM 4	R/V Hespérides	Mar–Apr, 2002	36.0° N-51.0° S
FICARAM 5	R/V Hespérides	Oct-Nov, 2002	37.4° N–23.1° S
FICARAM 6	R/V Hespérides	Apr, 2003	37.1° N–19.1° N
FICARAM 7	R/V Hespérides	Oct-Nov, 2004	37.3° N–55.1° S
FICARAM 8	R/V Hespérides	Oct-Nov, 2005	36.4° N–53.2° S
FICARAM 9	R/V Hespérides	Mar–Apr, 2006	32.4° N-55.1° S
FICARAM 10	R/V Las Palmas	Oct-Nov, 2006	37.4° N–53.2° S
FICARAM 11	R/V Las Palmas	Mar–May, 2007	37.5° N–54.8° S
FICARAM 12	R/V Las Palmas	Oct-Nov, 2007	36.0° N-62.9° S
FICARAM 13	R/V Las Palmas	Mar–Apr, 2008	37.4° N–55.1° S
FICARAM 14	R/V Las Palmas	Oct-Nov, 2008	37.5° N–62.9° S

**Table 1.** Information of the FICARAM cruises.

Notwithstanding its importance, air-sea CO<sub>2</sub> fluxes  $(FCO_2)$  are constrained rather poorly and introduce large uncertainties in global carbon budget estimates, particularly at interannual scales (Keeling et al., 1995; Francey et al., 1995; Battle et al., 2000, Schuster et al., 2009). This stems from the scarcity of in situ FCO<sub>2</sub> measurements and from the lack of time-series records. In order to improve our understanding of the ocean CO<sub>2</sub> uptake, it is essential to constrain the uncertainties associated with air-sea CO<sub>2</sub> fluxes  $(FCO_2)$  estimates both geographically and temporally. The Spanish project FICARAM (Air-sea CO<sub>2</sub> fluxes along meridional tracks in the Atlantic Ocean), was part of an international effort to carry out extensive in situ measurements at oceanic basin scales using available ship-potential. The FICARAM project was developed as repeat VOS line within the framework of larger European projects such as CAVAS-SOO (Carbon Variability Studies by Ships Of Opportunity) and CARBOOCEAN (Marine Carbon Sources and Sinks Assessment). The surface CO<sub>2</sub> observations collected during FICARAM are part of databases compiled by the projects CARBOOCEAN and SOCAT (Surface Ocean CO<sub>2</sub> Atlas).

The FICARAM cruises (Table 1) were carried out taking advantage of bi-annual ship tracks between Spain and the Antarctic from 2000 to 2008 providing a unique opportunity to get a quasi-synoptic view of a meridional transect in both the North and South Atlantic Oceans. These high-resolution observations helped showing the distribution over seasonal and long-term scales and mechanistic controls of surface seawater fugacity of CO<sub>2</sub> (fCO<sub>2</sub><sup>sw</sup>) within contrasting physicalchemical regimes (Keeling, 1968; Lefèvre, 1997) in spring and autumn. The diversity of oceanographic provinces sampled during the FICARAM cruises were marked and varied from highly productive areas located in upwelling systems to oligotrophic intertropical gyres. The cruise tracks also covered large areas in the North and South Atlantic Oceans, which are known to behave as important sinks of atmospheric CO<sub>2</sub> at present (Takahashi et al., 2009). The fluctuation in the major modes of climate variability, in particular, North Atlantic Oscillation (NAO), El Niño – Southern Oscillation (ENSO) and Southern Annular Mode (SAM) have been linked to observed anomalies of f CO<sub>2</sub> (Patra et al., 2005; Lovendruski et al., 2007; Borges et al., 2008) and other biochemical variables (Enfield and Mayer, 1997; Labat et al., 2005) in the Atlantic Ocean. In this sense, particular changes in the spatial f CO<sub>2</sub><sup>sw</sup> patterns of the North Atlantic Ocean were strongly related to the NAO index during the FICARAM period (Schuster and Watson, 2007; Schuster et al., 2009; Ullman et al., 2009)

In this paper, we summarize the underway  $f CO_2^{sw}$  measurements along a meridional transect of the Atlantic Ocean during the spring and autumn seasons since 2000 through 2008. The aim of this work is to characterize the differences of air-sea CO<sub>2</sub> fluxes and their biogeochemical forcing, and analyze the long-term trends observed in these variables during the FICARAM cruises.

### 2 Dataset and methods

### 2.1 The FICARAM cruises

The fourteen FICARAM cruises were conducted on board the research vessels *B/O Hespérides* and *B/O Las Palmas* beginning in October 2000 to November 2008 (Table 1). The cruise tracks covered approximately the same transit between the southern Spanish coasts and the Southern Ocean (Fig. 1). The heading of the courses was always southwards during the boreal autumn and northwards in boreal springs. The cruises were conducted as part of the Antarctic research program for maintenance and supplying the Spanish Antarctic



Fig. 1. Map showing the ship tracks and biogeochemical provinces selected for the FICARAM cruises. Left panel gives boreal spring tracks and right panel the boreal autumn ones.

bases Gabriel de Castilla and Juan Carlos I, located in the Deception and Livingston Islands, respectively.

The FICARAM cruises were principally conducted in the Eastern North and Western South Atlantic basins. Initially, cruises were intended to sail as close as possible to meridian  $28^{\circ}$ W while underway, but this was normally subject to ship-time availability. This practice ceased after the FICARAM 9 cruise, when the vessels started operating as ships of opportunity and sailed directly from departure to arrival ports. Nevertheless, sufficient cruises were conducted to study the meridional variability of  $f CO_2^{sw}$ .

#### 2.2 Equipment installation

The underway measurements of sea-surface and atmospheric molar fractions of  $CO_2$  ( $xCO_2^{sw}$  and  $xCO_2^{atm}$ , respectively) were performed with a GASPAR apparatus, an autonomous device assembled at Instituto de Investigacións Mariñas (IIM-CSIC, Vigo-Spain). The device configuration was based on a previous setup developed by researchers at the Institut für Meereskunde (Kiel – Germany; Körtzinger et al., 1996). The analytical principle is based on the equilibration of atmospheric air with the seawater sample under analysis.

There are several existing techniques available for achieving equilibration between a carrier gas phase and a seawater sample. The air – sea equilibrator system combines the advantages of a laminar flow system (Poisson et al., 1993) with a bubble-type system (Takahashi, 1961). The bubble equilibrator consists of a 1.5 L volume chamber through which surface seawater was being constantly pumped from 3 m under the waterline into the ship's hull through the ships nontoxic seawater supply system. The laminar flow equilibrator consisted of a 30 cm high glass column with two concentric cylinders to provide thermal insulation. The sampled seawater flowed at a rate of  $1.5-2 \text{ Lmin}^{-1}$  that was inputted from the top of the equilibrator's water chamber. A fixed volume of air was constantly recirculated through this system (0.8 Lmin<sup>-1</sup>) in order to favour rapid equilibration with the seawater phase. The system was vented to the atmosphere through an air ballast bottle flushed by an external airline stream which avoided enriched CO<sub>2</sub> air inputs from the laboratory.

A thermosalinograph (SBE-45-MicroTSG) was connected to the same uncontaminated seawater supply. This apparatus recorded underway surface temperature (SST) and salinity (SSS) during the cruises conducted on board *B/O Las Palmas*. When on board the *B/O Hespérides*, these data were gathered via the vessel-mounted oceanographic data acquisition system.

The molar fractions of CO<sub>2</sub> and H<sub>2</sub>O were measured with a non-dispersive infrared Li-COR analyser (model 6262) that is characterized by a stable drift over the long term. This precision experimental procedure is well documented and serves to determine the partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) in an airflushed equilibrator (Takahashi, 1961). The Li-COR instrument utilises a reference channel (apart from the measuring channel) where a dry CO<sub>2</sub>-free gas recirculates at a rate of  $0.2 \text{ L} \text{ min}^{-1}$ . Two standards were used through this channel, namely: a CO<sub>2</sub>-free air and a CO<sub>2</sub> standard gas of known concentration (375 ppm) certified by Instituto Meteorológico Nacional de Izaña (Canary Islands, Spain).

Gas mixtures were introduced in the Li-COR analyser via miniature solenoid valves, which were used to switch between gas inputs from various sources: atmospheric air, equilibrated air from the samples and the gas standards. A typical analytical cycle consisted of a calibration phase, which involved 20 measurements of each of the two gas standards. Immediately after calibration, the apparatus performs 24 uninterrupted sample measurements for about an hour, out of which 55 min were devoted to seawater equilibrated sample measurements and 5 min for atmospheric air records. The surface seawater observations were initially estimated with a 1-min frequency and averaged every 5-min cycle.

Remotely sensed chlorophyll *a* (chl *a*) was included in the presented FICARAM dataset as a proxy of the photosynthetic activity. Weekly fields of chl *a*, with a spatial resolution of 9 km<sup>2</sup> were remotely recorded by Sea-viewing Wide Field-of-view Sensor (SeaWIFS) Level 3 (Hooker et al., 1992) and downloaded from http://oceancolor.gsfc.nasa. gov/. The selected satellite records of chl *a* do not have an exact spatiotemporal match with ship measurements. Selection criteria for the choice of pixels consisted in considering only SeaWIFS measurements taken within  $\pm 4$  days (orbital over-passing) of the ship measurement date and found within  $\pm 6.3$  km off the track of the cruise.

# **2.3** Estimation of air and sea *f* CO<sub>2</sub> and air-sea CO<sub>2</sub> exchanges

The  $x CO_2^{\text{atm}}$  values were linearly interpolated versus latitude, using monthly measurements from selected meteorological stations of the NOAA/ESRL Global Monitoring Division located close to ship tracks (Fig. 1), namely: Mace Head (Ireland, 53.33° N), Azores (Portugal, 38.77° N), Izaña (Spain, 28.3° N), Ascension (UK, 7.92° S), Arembepe (Brazil, 12.77° S), Tierra de Fuego (Argentina, 54.87° S) and Palmer Station (US, 64.92° S). This dataset was preferred to in situ  $x CO_2^{atm}$  data due to the lack of these records during the last five cruises on board the B/O Las Palmas. For consistency, measurements from the NOAA/ESRL were used in all cases. The record gaps in the time-series from these stations were completed fitting the in situ  $x CO_2^{atm}$  recordings to a theoretical curve combining a seasonal cycle trend with the annual and semi-annual harmonics (Padin et al., 2007). The final  $x \text{CO}_2^{\text{atm}}$  dataset was then converted to  $p \text{CO}_2^{\text{atm}}$  (Eq. 1) considering the atmospheric pressure  $(p^{\text{atm}})$  and the partial pressure of water vapour (pH<sub>2</sub>O), which was calculated from in situ SST readings (Tis; Cooper et al., 1998) (Eq. 2). The  $pCO_2^{atm}$  values were then converted to  $fCO_2^{atm}$  assuming a decrease of 0.3% from the  $pCO_2^{\text{atm}}$  value (Weiss, 1974).

$$pCO_2^{atm} = xCO_2^{atm}(p^{atm} - pH_2O)$$
<sup>(1)</sup>

$$pH_2O = 0.981 \exp(14.32602 - (5306.83/(273.15 + T_{is}))) (2)$$

The measured  $xCO_2^{sw}$  data was converted to  $fCO_2^{sw}$  referenced to saturated water vapour pressure using in situ  $p^{atm}$  readings. The  $fCO_2^{sw}$  values were then corrected for the seawater temperature drift that occurs while the sample travels

from the hull's inlet into the equilibration chamber. This temperature shift was usually < 1 °C. The temperature tracking was done with platinum resistance thermometers and then applying the empirical equation proposed by Takahashi et al. 1993;  $\delta \ln p CO_2/\delta T = 0.04231 \degree C^{-1}$ ).

$$FCO_2 = kS\Delta fCO_2 \tag{3}$$

The  $FCO_2 \pmod{m^{-2} yr^{-1}}$  was calculated applying Eq. 3, where "S" stands for the solubility of  $CO_2$  in seawater (Weiss et al., 1974), "k" is the  $CO_2$  transfer velocity (Wanninkhof, 1992) and  $\Delta fCO_2 (\mu atm)$  is the air-sea  $fCO_2$  gradient (i.e.,  $fCO_2^{sw} - fCO_2^{atm}$ ). The coefficient "k" was computed using daily wind speed (WS) data obtained from NCEP-DOE AMIP-II Reanalysis (Kalnay et al., 1996). Data was accessed via the website of the NOAA-CIRES Climate Diagnostics Center, Boulder, Co, USA (http://www.cdc.noaa.gov/).

#### 2.4 Biogeochemical oceanographic provinces

The study of the meridional distribution of the  $f CO_2^{sw}$  measurements in the Atlantic Ocean (excluding the Mediterranean basin) focuses on selected biogeochemical provinces established after Longhurst et al. (1995) and Hooker et al. (2000). Different sections of the FICARAM tracks were allocated in the appropriate following ten regions according to average boundaries established from SST–SSS relationships (Fig. 1):

- (a) Eastern North Atlantic Subtropical Gyre (ENAS; 39° N–27° N) dominated by the Azores Current (Ríos et al., 1992) and comprising the northeast component of the North Atlantic Subtropical Gyre.
- (b) The Canary Current (CC; 27° N–16° N) is also part of the northern subtropical gyre with a moderate flow characterised by a salinity maximum that demarcates the beginning of the tropics. A coastal upwelling with a weak seasonality was located in the West African continental margin at these latitudes (Mittelstaedt, 1991).
- (c) The North Equatorial Current (NEC; 16° N–8° N) region is located amidst the zonal currents of the Equatorial Atlantic. This latitudinal band includes the Guinea Dome province (12° N–8° N), characterized by seasonal upwelling events that occur from December through May (Barton et al., 2001). At these latitudes, the chl *a* signal extends from the coast to the open oceans during the upwelling peak from February to May (Aristegui et al., 2009). During the summer this offshore growth of phytoplankton community abruptly drops.
- (d) The North Equatorial Counter Current province (NECC; 8° N-1° N) features a maximum flow from the easterly current during the Boreal Autumn that fades away during the winter and early spring (Richardson

and Reverdin, 1987). The seasonal changes in the location of the NECC were associated with the position of the InterTropical Convergence Zone. This province is also characterized by a band of low-density waters from the Amazon River with a core at  $4^{\circ}$  N– $5^{\circ}$  N (Müller-Karger et al., 1988) with SST values of ~25 °C and a SSS <35 (Emery & Dewar, 1982).

- (e) The *South Equatorial Current* province (SEC;  $1^{\circ}$  N- $15^{\circ}$  S) features a seasonal forcing with a maximum westward flow during the austral winter in the vicinity of the Equator. The South Equatorial Counter Current was weakly present between  $7^{\circ}$  S– $9^{\circ}$  S.
- (f) The South Atlantic Tropical Gyre province (STG; 15° S–31° S) exhibits relatively stable thermohaline properties with a gradual decrease of its SST and SSS values. An important poleward component of the Brazil Current that ran along the South American continental shelf is also present in this region.
- (g) The South American Shelf province (SAS; 31° S–40° S) is dominated by the Brazil Current as well, which extended southward as far as 44° S, in conjunction with a strong influence from the Plata river.
- (h) The South Atlantic Convergence zone (SAC; 40° S– 51° S) is a frontal area where the northward Falkland and southward Brazil currents converge. This characteristic generates high temperature gradients and large heterogeneity in the concentration fields of several chemical properties.
- (i) The *Falkland Current* (FC; 51° S–56° S) is a northward looping excursion of the Circumpolar Current that forms a jet of SST and SSS under 10 °C and 34.3, respectively (Bianchi et al., 1993).
- (j) The Drake Passage region, (DP; 56–66° S) extends from the southernmost tip of South America (56° S) to the northern tip of the Antarctic Peninsula (62° S). It is dominated by a racing eastward flow of the Antarctic Circumpolar Current. The Southern Ocean is characterized by a latitudinal succession of circumpolar frontal structures such as the Subantarctic Front, the Polar Front and the Continental Water Boundary.

A depth of 200 m was chosen as a boundary to separate ocean areas from shelf areas (Fig. 1). The CO<sub>2</sub> source-sink behaviour changes in the continental shelf with respect to deeper waters were also considered: while the distal shelf normally behaves as a CO<sub>2</sub> sink, the proximal shelf is essentially influenced by continental inputs and non-stratified conditions that favour the outgasing of CO<sub>2</sub> to the atmosphere (Thomas et al., 2004; Padin et al., 2007; Chen and Borges, 2009). Consequently, surface coastal waters (<50 m) that corresponded mainly to harbour areas were excluded from

the database. The ETOPO2v2 (USDC, NOAA, NGDC 2006) bathymetry was used for merging depth records using twodimensional linear interpolation functions of every measurement. After applying all of these selection criteria filters, a final FICARAM dataset comprising 67845 observations was put together.

### 3 Results

# 3.1 Overiew of the spatial variability of the FICARAM dataset

Figures 2 and 3 graphically depict the meridional distribution of SST, SSS,  $\Delta f CO_2$  and  $FCO_2$  measurements along the Atlantic Ocean (Fig. 1) during the spring and autumn seasons. Table 2 shows the mean values and the standard deviation of these variables including WS and chl *a* within the separated regions.

The meridional distribution of SST showed a clear interhemispheric symmetry that resulted from meridional differences in the Earth's radiation balance. Subtropical latitudes were characterized by spring-autumn differences of SST: during the boreal autumn, waters were warmer in the northern than in the southern hemisphere while during boreal spring, waters were warmer in the southern hemisphere compared to the Northern Hemisphere (Fig. 2a, c). The observed SST changes were negligible in the equatorial region between spring and autumn (Table 2). The spatial variability of the SSS measurements also showed an inter-hemispheric symmetry that disappeared in the Southern regions (Fig. 2b, d). Contrary to the SST distribution, the intense intertropical (23.4° S-23.4° N) precipitation rates reduce SSS values in the equatorial waters (Fig. 2b, d; Table 2) causing a clear minimum and reversing the direct SST-SSS relationship observed in the subtropical regions.

 $\Delta f CO_2$  variability in the Northern North Atlantic (Fig. 3b, d) loosely followed the seasonal SST changes. Lower values of  $f CO_2^{sw}$  compared to  $f CO_2^{atm}$  prevailed in the boreal spring (Table 2) while high  $f CO_2^{sw}$  values, which resulted in CO<sub>2</sub> oversaturation of the surface waters occurred during the boreal autumn. With the exception of the coastal regions, highest and lowest  $\Delta f CO_2$  values along the Atlantic Ocean were located in the SEC region and in the Patagonian Sea, respectively (Fig. 3b, d). FCO<sub>2</sub> estimations computed from  $\Delta f CO_2$  of the FICARAM dataset reproduced well the known behaviour of the tropical regions as sources of atmospheric  $CO_2$  and the seasonally shifting role of the subtropical ocean waters (Table 2). The Patagonian Sea permanently acted as sink of atmospheric  $CO_2$  reaching the strongest  $CO_2$ uptake along the FICARAM cruises in autumn (Fig. 3a, c; Table 2). Shelf waters sampled along the coasts of Africa and South America generally followed the behaviour of the adjacent ocean waters emphasizing the observed changes between spring and autumn with minor exceptions located in STG and FC regions (Table 2).

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Region	Boreal Season	Area	SST °C	SSS	chl a mg m <sup>-3</sup>	$\Delta f CO_2$	WS m s <sup>-1</sup>	$FCO_2$ mol m <sup>-2</sup> yr <sup>-1</sup>
	Deuson	shalf	$\frac{181+02}{181+02}$	$36.4 \pm 0.0$	$0.04 \pm 0.00$	-43 + 1	$69 \pm 0.7$	-20+00
<b>ENAS</b> 39–27° N	spring	ocean	$18.1 \pm 0.2$ $18.6 \pm 0.9$	$36.4 \pm 0.0$	$0.04 \pm 0.00$	-34 + 12	$74 \pm 25$	$-1.8 \pm 1.2$
		shelf	$10.0 \pm 0.9$ $22.0 \pm 0.6$	$36.0 \pm 0.2$ $36.5 \pm 0.2$	$0.11 \pm 0.07$ $0.15 \pm 0.06$	2 + 11	53+42	$1.0 \pm 1.2$ 0.3 ± 0.6
	autumn	ocean	$22.0 \pm 0.0$ $22.9 \pm 1.1$	$36.7 \pm 0.2$	$0.13 \pm 0.00$ $0.14 \pm 0.12$	$2 \pm 11$ 9 + 13	$5.3 \pm 4.2$ $5.2 \pm 2.7$	$0.3 \pm 0.0$ 0 2 + 0 4
		ahalf	194102	26.2 + 0.1	0.11 + 0.01	) ± 15	6 2 + 10	0.2 ± 0.1
CC	spring	sneif	$18.4 \pm 0.2$	$30.3 \pm 0.1$	$0.11 \pm 0.01$	10 + 12	$0.8 \pm 1.0$	14 - 10
27_16° N		ocean	$21.3 \pm 1.1$	$30.0 \pm 0.3$	$0.13 \pm 0.09$	$-19 \pm 13$	$8.9 \pm 1.4$	$-1.4 \pm 1.0$
27-10 1	autumn	ocean	$25.3 \pm 1.5$	$36.7 \pm 0.4$	$0.12 \pm 0.06$	16±13	$6.6 \pm 2.6$	0.6±0.5
NEC	spring	ocean	$24.9 \pm 1.3$	$35.9\pm0.2$	$0.13 \pm 0.07$	$-17 \pm 10$	$7.6 \pm 1.8$	$-0.7 \pm 0.4$
16–8° N	autumn		$28.1\pm0.6$	$35.7 \pm 0.4$	$0.12\pm0.06$	$2\pm14$	$6.1\pm2.0$	$0.0 \pm 0.5$
NECC	spring	ocean	$28.1\pm0.5$	$35.6\pm0.3$	$0.14\pm0.08$	$1\pm 16$	$5.5\pm1.7$	$0.1 \pm 0.4$
8–1° N	autumn	ocean	$28.2\pm0.6$	$35.1\pm0.5$	$0.11\pm0.04$	$3\pm13$	$4.5\pm1.8$	$0.1\pm0.3$
<b>SEC</b> 1° N–15° S		shelf	29.1±0.3	$37.0 \pm 0.2$	$0.17 \pm 0.01$		$2.0 \pm 0.2$	
	spring	ocean	$28.7\pm0.3$	$36.3\pm0.6$	$0.18\pm0.08$	$30\pm11$	$4.2\pm2.0$	$0.7\pm0.5$
		shelf	$27.1\pm0.3$	$36.5\pm0.2$	$0.16\pm0.04$	$34\pm8$	$7.1\pm1.1$	$1.6\pm0.6$
	autumn	ocean	$26.8\pm0.5$	$36.3\pm0.3$	$0.14\pm0.05$	$24\pm12$	$7.0\pm1.6$	$1.0\pm0.7$
<b>STG</b> 15–31° S		shelf	$26.3 \pm 1.5$	$36.4 \pm 0.5$	$0.15\pm0.05$	17±17	5.0±1.5	$0.4 \pm 0.4$
	spring	ocean	$27.4 \pm 1.0$	$36.9\pm0.3$	$0.17\pm0.06$	$21\pm14$	$5.8 \pm 1.9$	$0.6\pm0.6$
	autumn	shelf	$23.8 \pm 1.5$	$36.5\pm0.5$	$0.13\pm0.02$	$14\pm9$	$8.6\pm3.2$	$0.5\pm0.7$
		ocean	$23.9 \pm 1.7$	$36.8\pm0.4$	$0.17\pm0.07$	$-5\pm17$	$6.9 \pm 1.7$	$-0.2\pm0.7$
		shelf	$22.1 \pm 2.0$	$33.2 \pm 2.2$	$0.28 \pm 0.16$	$-19 \pm 27$	$5.4 \pm 2.7$	$-0.7 \pm 1.3$
SAS	spring	ocean	$20.7 \pm 4.1$	$35.0 \pm 1.1$	$0.24\pm0.10$	$-28\pm30$	$6.1 \pm 2.8$	$-0.9 \pm 1.5$
SAS 31–40° S	autumn	shelf	$14.9\pm2.5$	$32.6 \pm 1.1$	$0.18\pm0.09$	$-67\pm37$	$7.4\pm2.2$	$-3.2 \pm 2.7$
		ocean	$17.8 \pm 1.8$	$35.6\pm0.5$	$0.11\pm0.04$	$-41\pm16$	$7.1\pm3.1$	$-2.2\pm2.1$
		shelf	$10.4 \pm 0.6$	<i>33.6</i> ±0.1	$0.26 \pm 0.05$	$-42 \pm 9$	$9.0 \pm 1.1$	$-3.2 \pm 1.1$
<b>SAC</b> 40–51° S	spring	ocean	$11.9 \pm 2.2$	$34.0\pm0.2$	$0.26\pm0.10$	$-39\pm16$	$7.4 \pm 3.8$	$-1.9 \pm 2.1$
	autumn	shelf	$9.5\pm2.1$	$33.4\pm0.3$	$0.11\pm0.03$	$-70\pm42$	$8.2\pm3.4$	$-4.1 \pm 4.0$
		ocean	$9.3\pm1.4$	$33.8\pm0.1$	$0.15\pm0.06$	$-57\pm26$	$9.9\pm3.1$	$-5.4\pm3.6$
FC	spring	shelf	9.2±0.6	<i>33.3</i> ±0.3	$0.40 \pm 0.15$	$-7 \pm 23$	$10.8 \pm 4.8$	$-0.7 \pm 2.8$
		ocean	$8.8 \pm 0.5$	$33.6 \pm 0.2$	$0.43 \pm 0.22$	$1\pm 26$	$10.6 \pm 5.3$	$1.2 \pm 2.5$
		shelf	$6.6\pm0.8$	$32.9\pm0.5$	$0.09\pm0.04$	$-15\pm32$	$10.4\pm3.0$	$-1.4 \pm 3.2$
J1-JU S	autumn	ocean	$6.8\pm1.1$	$33.6\pm0.4$	$0.08\pm0.02$	$-50\pm40$	$9.7\pm3.5$	$-2.8\pm2.5$
DP		shelf	$-0.8 \pm 0.7$	$34.1 \pm 0.1$	$0.14 \pm 0.05$	$8 \pm 14$	3.9±1.6	0.1±0.3
56–66° S	autumn	ocean	$1.3\pm2.3$	$33.8\pm0.2$	$0.10\pm003$	$-20\pm11$	$6.8\pm3.0$	$-1.1\pm0.9$

**Table 2.** Statistics for the selected provinces on the different boreal seasons (spring; autumn) and areas (shelf; ocean): Mean and standard deviation ( $\mu \pm \sigma$ ) of SST, SSS, chl *a*,  $\Delta f CO_2$ , WS,  $F CO_2$ .



Fig. 2. Latitudinal distributions during boreal springs (a, b) and boreal autumns (c, d) of SST and SSS as measured in the FICARAM cruises.



Fig. 3. Latitudinal distributions during boreal springs (a, b) and boreal autumns (c, d) of  $FCO_2$  and  $\Delta fCO_2$  as measured in the FICARAM cruises.

### **3.2** Observed distribution of biogeochemical variables in the Atlantic provinces

*Eastern North Atlantic Subtropical Gyre* (ENAS): Equatorward warming and modest increase in SSS characterized the surface waters of the ENAS province during spring and autumn seasons (Fig. 2). The seasonal variability of the SST observations that reached 4.3 °C in the ocean waters and was the largest observed in the Atlantic Ocean (Table 2). On the contrary, SSS measurements in April and autumn closely agreed to an average value of 36.6 showing a change lower than 0.1 (Table 2).

Ocean waters of the ENAS region were considerably undersaturated during spring in relation to the atmosphere  $(-34 \pm 12 \,\mu \text{atm})$  and sligthly oversaturated in autumn  $(9 \pm 13 \,\mu \text{atm})$ . This spring–autumn shift of  $\Delta f \text{CO}_2$ of 43  $\mu$ atm was the highest observed among the regions of the North Atlantic Ocean. Hence oceanic waters acted as a considerable sink of atmospheric CO<sub>2</sub> of  $-1.8 \pm 1.2 \,\text{mol}\,\text{m}^{-2}\,\text{yr}^{-1}$  in April and a small CO<sub>2</sub> source of  $0.2 \pm 0.4 \,\text{mol}\,\text{m}^{-2}\,\text{yr}^{-1}$  in autumn. The *F*CO<sub>2</sub> exchange in coastal waters essentially mirrored those observed in open ocean waters with a slight intensification. So, the surface waters of the shelf region showed the largest seasonal span in the *F*CO<sub>2</sub> ranging from  $-2.0 \pm 0.0 \,\text{mol}\,\text{m}^{-2}\,\text{yr}^{-1}$  and  $0.3 \pm 0.6 \,\text{mol}\,\text{m}^{-2}\,\text{yr}^{-1}$  in spring and autumn (Table 2), respectively. The *Canary Current* (CC): The dataset collected in the CC region also revealed the increase of SST and  $\Delta f CO_2$  to the south, as was observed in the ENAS region. The surface waters were appreciably warmer than surface waters found in the ENAS region by 2.7 °C and 2.4 °C during spring and autumn, respectively. On the contrary a SSS decrease from a maximum value located at around 27° N was also observed during both seasons in parallel with the equatorward warming. Similarly to the surface waters of the ENAS region, the CC region acted as a CO<sub>2</sub> sink  $(-1.4 \pm 1.0 \text{ mol m}^{-2} \text{ yr}^{-1})$  in spring and a modest CO<sub>2</sub> source of  $0.6 \pm 0.5 \text{ mol m}^{-2} \text{ yr}^{-1}$  in autumn.

The effects of the upwelling events were observed in the cruises conducted closer to the coast at these latitudes. As a result,  $\Delta f CO_2$  values of up to 50 µatm during autumn (Fig. 3d) were found at around 20° N associated with the cold upwelled water (Fig. 2b). In the same region, an intense CO<sub>2</sub> undersaturation exceeding  $-50 \mu$ atm was also found along the Mauritanian coast (Fig. 3d) coincident with an intense photosynthetic activity. Remotely sensed chl *a* observations revealed values of 1.3 mg m<sup>-3</sup> (data not shown).

The North Equatorial Current (NEC): The surface waters of the NEC region supported the equatorward warming and the decrease of SSS observed in the CC region. On the other hand,  $\Delta f CO_2$  measurements (Fig. 2) did not follow the meridional distribution. Surface waters during spring showed an underaturation of  $-17 \pm 10 \mu \text{atm}$  (Table 2) in spring and a value of  $2 \pm 14 \mu \text{atm}$  in autumn pointing out equilibrium CO<sub>2</sub> situation with the atmosphere of these waters after summer.

The North Equatorial Counter Current province (NECC): North of the equator, a distinct wide band of low SSS values characterized the surface waters of the NECC province. These less saline waters of the ocean waters reached the lowest mean value of  $35.1 \pm 0.5$  of the North Hemisphere in March–April showing an outstanding SSS shift of 0.5 from spring to autumn. Conversely the seasonal variability of SST that reached the highest value in boreal autumn season of  $28.2 \pm 0.6$  °C was practically absent and the spring–autumn range of  $\Delta f CO_2$  and  $FCO_2$  also showed minimal variability. The NECC waters acted as small CO<sub>2</sub> sources to the atmosphere in both seasons (Table 2) with mean values of  $0.1 \text{ mol m}^{-2} \text{ yr}^{-1}$  estimated from  $\Delta f CO_2$  of  $1 \pm 16$  and  $3 \pm 13$  µatm in spring and autumn, respectively.

The South Equatorial Current (SEC): Average SST values of  $29.1 \pm 0.3$  and  $28.7 \pm 0.3$  °C in spring characterised the shelf and ocean areas of the SEC as having the warmest waters along FICARAM cruises (Table 2). The ocean waters also showed the highest CO<sub>2</sub> supersaturation in spring and autumn with  $\Delta f CO_2$  values of  $30 \pm 11$  and  $24 \pm 12 \mu atm$ , respectively. Despite these observations, a stronger CO<sub>2</sub> outgassing of  $1.0 \pm 0.7 \text{ mol m}^{-2} \text{ yr}^{-1}$  was estimated in autumn because of the relatively higher wind speeds of  $7.0 \pm 1.6 \text{ m s}^{-1}$ . In any case, SEC waters were the most

important sources of  $CO_2$  to the atmosphere in the current study.

The South Atlantic Tropical Gyre province (STG): The subtropical waters of the South Hemisphere showed notable changes from spring to autumn that were opposite to those of the North Atlantic. The distribution of SST and SSS showed a direct correlation. Both variables showed a poleward declination that reflects the heat loss of waters and the influence of continental inputs (Fig. 2). This pattern was closely repeated in the  $\Delta f CO_2$  distribution (Fig. 3b, d). Mean  $\Delta f CO_2$  values of the ocean waters were  $21 \pm 14 \,\mu atm$ in March–April and  $-5 \pm 17$  µatm in October-November and so, they acted as a source of  $0.6 \pm 0.6 \text{ mol m}^{-2} \text{ yr}^{-1}$  in spring and as a small sink of  $-0.2 \pm 0.7 \text{ mol m}^{-2} \text{ yr}^{-1}$  in autumn (Table 2). The distal shelf of Brazil coast at these latitudes was a slight CO<sub>2</sub> source in both seasons of  $0.4 \pm 0.4$ and  $0.5 \pm 0.7 \text{ mol m}^{-2} \text{ yr}^{-1}$  in the period March-April and October-November, respectively (Table 2).

The South American Shelf province (SAS): The recordings in this region were mostly confined to the South American continental shelf that allowed the clear influence of inputs from the River Plate. The fluvial discharges decreased SSS to  $32.6 \pm 1.1$  in November which was the lowest value along the Atlantic Ocean. The shelf and ocean waters of the SAS region were strongly undersaturated and acted as a strong CO<sub>2</sub> sink during both seasons (Fig. 3). The CO<sub>2</sub> undersaturation was especially intense over the shelf-break in November reaching  $\Delta f CO_2$  values lower than -190 µatm (Fig. 2g) and an average CO2 absorption of  $-3.2 \pm 2.7 \text{ mol m}^{-2} \text{ yr}^{-1}$  (Table 2). During the same month, oceanic waters showed a CO2 sink with a strength of  $-2.2 \pm 2.1 \text{ mol m}^{-2} \text{ yr}^{-1}$ . The CO<sub>2</sub> uptake of the surface waters in March showed SST values up to 20 °C was  $-0.9\pm1.5\,mol\,m^{-2}\,yr^{-1}$  and  $-0.7\,mol\,m^{-2}\,yr^{-1}$  in the ocean and coastal waters, respectively (Table 2).

The South American Convergence zone (SAC): The confluence of the warm and saline Brazil Current and the cold and less saline Falkland Current at these latitudes caused relatively high spatial heterogeneity of SSS and SST distributions (Fig. 2). This region showed relatively strong changes in the SST and SSS distribution that reached ~6°C and ~2 during FICARAM 7 (Fig. 2). In spite of this variability, these waters acted as very strong sink of atmospheric CO<sub>2</sub> during both seasons as found in the SAS region. The strongest undersaturation of the ocean waters of  $-57 \pm 26 \,\mu atm$  in November modulated by an intense WS of  $9.9 \pm 3.1 \,\mathrm{m \, s^{-1}}$  resulted in  $FCO_2$  value of  $-5.4 \pm 3.6 \,\mathrm{mol \, m^{-2} \, yr^{-1}}$  (Table 2). This was the highest CO<sub>2</sub> uptake estimated along the Atlantic Ocean for this study (Fig. 3c).

The *Falkland Current* (FC): Oceanic waters of the FC region in March were slightly supersaturated in  $CO_2$  by  $1 \pm 26 \mu atm$  in spite of high chl *a* value of  $0.43 \pm 0.22 \text{ mg m}^{-3}$ . The  $\Delta f CO_2$  values close to the airsea equilibrium observed through the "furious fifties" of the Southern Ocean with WS up to  $10 \text{ m s}^{-1}$  resulted in  $CO_2$ 

outgassing of  $1.2 \pm 2.5 \text{ mol m}^{-2} \text{ yr}^{-1}$  (Table 2). In November, the same area reversed its role becoming a large CO<sub>2</sub> sink of  $-2.8 \pm 2.5 \text{ mol m}^{-2} \text{ yr}^{-1}$ . Shelf waters did not exhibit the same seasonal shift and acted as a sink of CO<sub>2</sub> during both seasons (Table 2). The CO<sub>2</sub> uptake of these waters in November was estimated at  $-1.4 \pm 3.2 \text{ mol m}^{-2} \text{ yr}^{-1}$  during autumn in association with low SSS values of  $32.9 \pm 0.5$  (Fig. 2d; Table 2). More saline waters ( $33.3 \pm 3$ ) on the shelf area were found in March showing a CO<sub>2</sub> absorption of  $-0.7 \pm 2.8 \text{ mol m}^{-2} \text{ yr}^{-1}$ .

The *Drake Passage* region (DP): These waters of the Southern Ocean were only sampled in November 2007 and 2008. The meridional distribution in this branch of the Southern Ocean showed a marked thermohaline distribution with two strong gradients at  $\sim 57^{\circ}$  S and  $\sim 58.7^{\circ}$  S. These features represent the known zonation of Antarctic waters, that is, the Subantarctic Front and the Polar Front, respectively, delimiting the Antarctic Circumpolar Current. This pattern was narrowly repeated in the four cruises during both autumns (Fig. 2). In the shelf waters of the Livingston Island, SST had a mean value of  $0.8 \pm 0.7 \,^{\circ}$ C (Table 2) which was the lowest one along the Atlantic Ocean. To the south of the Polar Front, SSS showed a clear onshore increase (Fig. 2d).

Opposite values in the CO<sub>2</sub> saturation in relation to the atmosphere were found in the shelf and ocean waters. Ocean waters were undersaturated with values of  $-10 \pm 4 \mu atm$  in November 2007 and  $-21 \pm 21 \mu atm$  during November 2008. The stronger undersaturation of 2008 was characterized by a southward intensification along the Drake Passage reaching a minimum value around  $-80 \mu atm$  at  $\sim 62^{\circ}$  S. Surface waters over the distal shelf showed an average oversaturation of  $8 \pm 14 \mu atm$  (Fig. 3d; Table 2) that followed an onshore increase similar to the SSS distribution. Therefore ocean waters of the Southern Ocean along the Drake Passage acted as a sink of  $-1.1 \pm 0.9 \text{ mol m}^{-2} \text{ yr}^{-1}$  while coastal waters released CO<sub>2</sub> to the atmosphere with a mean rate of  $0.1 \pm 0.3 \text{ mol m}^{-2} \text{ yr}^{-1}$  during the successive November (Table 2).

### 3.3 Long-term trend in biogeochemical variables during the FICARAM cruises from 2000 to 2008

The long-term trends from years 2000 to 2008 of the variables measured and estimated from the database gathered during the FICARAM cruises were studied from the interannual changes in each province (Fig. 4). These temporal changes were only evaluated in oceanic waters in order to avoid the high susceptibility of coastal waters to anthropogenic and climatic forcing (Wolf-Gladrow et al., 1999; Anderson and Mackenzie 2004; Bakun et al., 2010). In addition data from the Western basin of the North Atlantic Ocean that were only sampled during spring 2007 (Fig. 1) were excluded due to the differences with the Eastern basin (Lüger et al., 2004). Furthermore we assume the influence of the longitudinal variability of the FICARAM tracks on the longterm trends was almost null. The mean values of every variable were linearly fitted to identify significant decadal trends (p < 0.05) during the successive springs and autumns. These interannual trends should only be taken into account as year-to-year trends of these seasons due to the seasonal variability of the long-term variability (Lefevre et al., 2004; Padin et al., 2009).

The provinces of the North Atlantic Ocean (Fig. 4a, b and c) showed an appreciable but not significant warming of the surface waters during the cruises of spring and autumn seasons. In addition to the observed long-term trend of SST, the subtropical surface waters roughly pointed out a slight increase of  $\Delta f CO_2$  and a weakening of the oceanic uptake of  $CO_2$  (Fig. 4a, b, and c) as well. Other variables with a direct influence on the air-sea  $CO_2$  exchange showed highly statistically significant changes in the subtropical waters. Thus, a declination of the WS of  $-0.30 \pm 0.07 \text{ m s}^{-1} \text{ yr}^{-1}$  was found in the CC province during the successive spring cruises (Fig. 4b) that was also accompanied by a minor decrease in SSS. The spring chl *a* distribution also showed a significant interannual trend of  $-0.3 \pm 0.1 \text{ mg m}^{-3} \text{ yr}^{-1}$  (Fig. 4c) in the NEC province.

Significant interannual changes were particularly pronounced in the equatorial regions. The NECC region showed a sustained decrease of  $-0.16 \pm 0.01 \, \text{yr}^{-1}$  in SSS during the autumn season (Fig. 4d). Besides the observed SSS drop, an increase of the undersaturation in  $CO_2$  of  $-3.5 \pm 0.9 \,\mu atm \, yr^{-1}$  and of the ocean  $CO_2$  uptake of  $-0.09 \pm 0.03$  mol m<sup>-2</sup> yr<sup>-2</sup> characterized the NECC province. To the south of the equator, the tropical waters of SEC province showed a significant warming of  $0.11 \pm 0.03$  °C yr<sup>-1</sup> during the successive autumn cruises that was the only interannual SST change found along the Atlantic Ocean. Apart from this significant warming, the interannual WS variation also showed a noteworthy decrease of  $-0.58 \pm 0.14$  m s<sup>-1</sup> yr<sup>-1</sup> during the same season. It is noticeable that, in general terms, the trend observed in  $\Delta f CO_2$ and  $FCO_2$  in the equatorial regions was opposite to the ones found in the subtropical latitudes.

On the Patagonian Sea, the surface waters of the SAS and SAC regions during consecutive spring seasons were also influenced by a drop in WS of  $-0.50 \pm 0.11 \text{ m s}^{-1} \text{ yr}^{-1}$  and of  $-1.24 \pm 0.26 \text{ m s}^{-1} \text{ yr}^{-1}$ , respectively (Fig. 4g, h).

# **3.4** Analysis of the biogeochemical forcing on the $f \operatorname{CO}_2^{\operatorname{sw}}$ variability

The correlations between  $f CO_2^{sw}$  and the ancillary parameters in the ocean waters were explored to identify the processes controlling  $f CO_2^{sw}$  variability during the FICARAM cruises. These  $f CO_2^{sw}$  measurements were modelled with an empirical algorithm according to biochemical forcing (Olsen et al., 2004; Ono et al., 2004; Wanninkhof et al., 2007; Lueger et al., 2008; Padin et al., 2008). Spring and autumn measurements were separated as in the study of long-term



**Fig. 4.** Temporal variation of the averaged SST, SSS, chl *a*, WS,  $\Delta f CO_2$  and  $FCO_2$  cruise (error bars stand for the respective standard deviation) in each of the selected biogeochemical provinces. Spring and autumn values are shown as dark and open circles, respectively. Significant regression lines (p < 0.05) and regression slopes including the standard error are also given. Solid lines stand for spring results and dashed lines for autumn.

variability. Prior to making this analysis, all measurements were referenced to their respective months in the year 2005, which was arbitrarily chosen as the reference year. This adjustment consisted of adding or subtracting to each sample the  $xCO_2^{atm}$  difference between the date of the measurement and the one in 2005 as described in Sect. 2.3. The effect

of temperature on the  $f \operatorname{CO}_2^{\operatorname{sw}}$  measurements was removed by normalising the observations to the mean in situ SST (Table 2) following Takahashi et al. (1993). This new normalised and corrected variable ( $f \operatorname{CO}_2^{\operatorname{sw}}$ ) was then used to estimate the biochemical control. The  $f \operatorname{CO}_2^{\operatorname{sw}}$  values were fitted with second-order multiple polynomials using SST and chl *a* observations as described in Ono et al. (2004) and linear relationship with SSS and WS as independent variables according to the Eq. 4.

$${}^{\prime}f \operatorname{CO}_{2}^{\operatorname{sw}} = \operatorname{A} + \sum_{i=1}^{2} \varphi_{i} \left(\operatorname{SST} - \mu_{\operatorname{SST}}\right)^{i} + \operatorname{B}(\operatorname{SSS} - \mu_{\operatorname{SSS}}) \qquad (4)$$
$$+ \operatorname{CWS} + \sum_{i=1}^{2} \beta_{i} \left(\operatorname{chl} a\right)^{i}$$

The multiple linear regression coefficients were obtained using a forward stepwise method where only parameters that accounted for at least 1% of the ' $f CO_2^{sw}$  variability were included in the algorithm. The  $\mu_{SST}$  and  $\mu_{SSS}$  stand for averages value of SST and SSS for each province, respectively (Table 2). The regression coefficients for (4) and the percentage of normalized  $f CO_2^{sw}$  variability explained by each parameter in the different provinces are given in Table 3.

The empirical algorithm explained most of the ' $f \text{CO}_2^{\text{sw}}$  variability of the separated provinces along the Atlantic Ocean. The  $f \text{CO}_2^{\text{sw}}$  changes observed in regions during spring and summer were correctly fitted and the root mean square errors ranged between 7.1 and 31.9 µatm estimated in the ENAS and SAC regions, respectively, in autumn (Table 3).

The main driver of the  $f \text{CO}_2^{\text{sw}}$  variability was SST in practically every region, with the exception of the surface waters of the equatorial provinces such as NEC in autumn and NECC during both seasons. SST was especially the main parameter explaining ' $f \text{CO}_2^{\text{sw}}$  variability in the subtropical waters of both hemispheres reaching a maximum value of 85% in SAC region. The SST-' $f \text{CO}_2^{\text{sw}}$  correlations were mostly negative due to the lower pH values in warmer waters. Strong SST-' $f \text{CO}_2^{\text{sw}}$  relationships were observed in the provinces characterized by the upwelling and mixing of different waters (Table 3). As a result, the strongest relationships were found in the upwelling systems of the equator waters (SEC province in autumn;  $-34 \pm 3 \,\mu \text{atm} \,^\circ \text{C}^{-1}$ ) and of the Southern Ocean (FC in March;  $-84 \pm 3 \,\mu \text{atm} \,^\circ \text{C}^{-1}$ ).

In general terms, the effect of the observed SSS changes on  ${}^{*}f \text{CO}_{2}^{\text{sw}}$  was secondary. However the  ${}^{*}f \text{CO}_{2}^{\text{sw}}$  variability of tropical waters in autumn showed an important dependence of the SSS changes. The influence of SSS on  $f \text{CO}_{2}^{\text{sw}}$  reached a maximum value of 79% in the NECC region with a coefficient of  $17.3 \pm 0.3 \,\mu$ atm per SSS unit (Table 3). The SSS also accounted for 49% of the observed  ${}^{*}f \text{CO}_{2}^{\text{sw}}$  variability in spring in which the SSS minimum was located (Table 2). On the north,  ${}^{*}f \text{CO}_{2}^{\text{sw}}$  changes of the NEC region reproduced a similar seasonal influence of SSS explaining 11% and 62% in spring and autumn, respectively. The contribution of the SSS to the  $f \text{CO}_{2}^{\text{sw}}$  variability was also notable in the surface waters of the DP reaching an 10%.

Phytoplankton activity estimated via the chl *a* proxy showed a reduced influence on the ' $f \operatorname{CO}_2^{\operatorname{sw}}$  variability that did not exceed 7%. This percentage was obtained in the

ENAS region with a coefficient of  $-11.0 \pm 0.5 \,\mu$ atm mg m<sup>-3</sup> in autumn. Other regions sampled in the vicinity of the coastline such as STG and SAS region also showed a significant inverse ' $f \text{CO}_2^{\text{sw}}$ -chl *a* relationship that pointed out an important biological CO<sub>2</sub> uptake (Table 3). Remotely sensed chl *a* also had a notable influence on the  $f \text{CO}_2^{\text{sw}}$  of the FC region. However contrary to expectation, similar positive correlations between  $f \text{CO}_2^{\text{sw}}$ -chl *a* of  $61 \pm 11$  and  $67 \pm 19 \,\mu$ atm mg m<sup>-3</sup> were observed in March and November, respectively.

#### 4 Discussion

The fourteen FICARAM cruises held between 2000 and 2008 have allowed us analyze the  $f CO_2^{sw}$  variability over seasonal and long-term scales and its biochemical forcing in spring and autumn. These underway measurements revealed a consistent pattern in the Northern Hemisphere but larger variability in the South Hemisphere (Figs. 2, 3) coinciding with the finding of Gruber et al. (2009) from analyzing anthropogenic fluxes. The consistency of these underway observations gathered on board of R/V Hespérides and R/V Las Palmas was studied comparing them with the recent climatology produced by Takahashi et al. (2009) (hereinafter; TC09). It is necessary to clarify that these cruises were not included in the construction of TC09 as other measurements calibrated with two standard gases (see Sect. 2.2). The colocation criteria of the monthly TC09 estimations meant that they did not differ temporally by more than 15 days and spatially by more than 355 km. The differences of  $\Delta f CO_2$  between those measured in the FICARAM cruises and TC09  $(\Delta \Delta f CO_2)$  were corrected by taking into account the SST disagreements ( $\Delta$ SST) and estimating  $\Delta \Delta f$ CO<sub>2</sub>. The adjustment was carried out assuming theoretical temperature dependence in isochemical conditions such as described in Takahashi et al. (1993). Climatological k and S according to Eq. 3 multiplied  $\Delta \Delta f CO_2$  in order to obtain  $FCO_2$  differences between both datasets ( $\Delta FCO_2$ ). Table 4 shows the mean and standard deviation of these differences with the disagreements in SST ( $\Delta$ SST) and SSS ( $\Delta$ SSS).

In general terms, the FICARAM dataset showed warmer surface waters along the Atlantic Ocean with the exception of the Patagonian Sea than the reported by TC09 (Table 4). These disagreements were higher during the spring cruises reaching significant offsets. On the contrary,  $\Delta$ SSS values were minimum with the exception of NECC and regions of the Patagonian Sea which are characterized by a large continental inputs and complex oceanography (Wanninkhof et al., 2007; Bianchi et al., 2009) and in which FICARAM cruises sampled less saline waters.  $\Delta f CO_2$  values along the Atlantic Ocean showed a statistically insignificant mean anomaly of  $-3 \pm 18 \mu atm$ . This intensification in the CO<sub>2</sub> undersaturation yielded a small increase of  $0.02 \pm 0.14 \text{ mol m}^{-2} \text{ yr}^{-1}$  of the ocean uptake of atmospheric CO<sub>2</sub>. In general terms, these

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Region	Season	rms	'fCO <sub>2</sub>	sst-µ	(sst-µ) <sup>2</sup>	sss-µ	WS	chl a	chl $a^2$
		µatm	µatm n	$^{\circ}C$ $r^{2'}$	$^{\circ}C^{2}$		$(m s^{-1})$	$(mg m^{-3})$	$(mg m^3)^2$
	spring	9.2	361 ± 1	$-15.2 \pm 0.9$		$25\pm1$	$-0.9 \pm 0.1$		$3.8 \pm 0.4$
ENAS			2739	60		3	2		1
39–27° N	autumn	71	$372.9\pm0.4$	$-6.8\pm0.3$	$-0.9\pm0.1$			$-11.0\pm0.5$	
	uutuiiii	/.1	5759	68	1			7	
	spring	11.8	$337\pm2$	$-19\pm1$	$-1.6\pm0.2$	$6.5\pm0.7$	$3.1\pm0.2$		$9.1\pm0.7$
СС	spring	1110	1879	48	2	2	6		2
27–16° N	autumn	13.3	$402.4\pm1$	$-16.9\pm0.1$	$0.82\pm0.07$	$5.7\pm0.4$	$-1.3\pm0.1$	$-83\pm3$	$47\pm2$
	uutuiiii	15.5	6091	74	1		1	1	1
	spring	10.4	$356\pm 2$	$-13.8 \pm 8$		$41 \pm 1$			
NEC	spring	10.4	685	<i>79</i>		11			
16–8° N	autumn	13.2	$357\pm1$	$-5.7\pm0.3$	$4.5\pm0.6$	$24.2\pm0.4$	$-0.9\pm0.1$	$73 \pm 4$	$-72\pm5$
	autumn	13.2	3734	4	1	62	1	1	3
	annina	0.1	$308 \pm 1$	$19\pm 1$	$4.6\pm0.9$	$34 \pm 1$	$4.5 \pm 0.3$		-21±5
NECC	spring	9.1	903	15	2	49	6		1
8–1° N	outumn	78	$345.2\pm0.4$	$-16 \pm 0.3$		$17.3\pm0.3$	$2.0\pm0.1$	$48 \pm 3$	
o-1 in autu	autuiiii	7.0	3778	7		79	3	1	
sp:	annina	10.7	$398 \pm 4$	$-34 \pm 3$	$6\pm 1$	$-8.5\pm0.6$	$2.3 \pm 0.2$		
	spring	10.7	1586	28	1	7	6		
1° N–15° S	outumn	12.8	$379 \pm 1$	$-29.3\pm0.5$		$-23.7\pm0.5$			
1 10 10 0	autumm		6169	36		16			
spri STG 15–31° S autu	enring	12.2	$351\pm8$		$-1.9\pm0.1$	$-18.3 \pm 0.6$			83±9
	spring	12.2	3164		56	11			1
	autumn	13.6	$389 \pm 1$	$-12.5\pm0.2$		$7.1\pm0.6$	$-1.1\pm0.1$	$-49\pm2$	$14\pm 1$
	uutunni		4212	58		1	1	4	2
	spring	13 /	$325.6\pm0.5$	$-8.8 \pm 1.1$	$0.59\pm0.03$				
SAS	spring	lg 15.4	1584	81	4				
31–40° S	autumn	umn 19.5	$380\pm4$	$-4.3\pm0.5$		$2.0\pm0.4$	$-2.8\pm0.2$	$-157\pm32$	
			2434	23		1	7	6	
<b>SAC</b> 40–51° S	spring	ng 17.5	$355\pm1$	$-22.9\pm0.2$	$1.00\pm0.03$	$30 \pm 1$			$87\pm7$
			1893	85	4	2			1
	outumn	ın 31.9	$340\pm8$	$68 \pm 4$	$16.2\pm0.8$	$104\pm8$	$7.0\pm0.6$		
	autuiliii		593	6	47	14	8		
	enring	16.0	$386\pm 6$	$-34\pm3$	$-6\pm 2$		$-2.3\pm0.3$	$61\pm11$	
FC	spring		329	69	4		3	4	
51–56° S	autumn	24.0	$327\pm5$	$-84\pm3$	$-21\pm2$	$21\pm 2$	$-3.5\pm0.3$	$67\pm19$	
51-56° S		24.0	709	69	8	5	5	1	
DP	outree	10.1	339±3	$-14.1 \pm 0.2$		86±3		$312\pm42$	
 56 66° S	autumn	12.4	1415	75		10		1	

**Table 3.** Regression coefficients (in italics) and variability explained (bold-faced) by each of the parameters included in the empirical algorithm given in equation (4) applied in every biogeochemical province where  $f \operatorname{CO}_2^{\operatorname{sw}}_0$  mean the start point. The root mean square (rms) and the correlation coefficient ( $r^2$ ) are also given. The "n" value stands for the number of valid data included in each analysis.

**Table 4.** Mean differences and standarad deviation ( $\mu \pm \sigma$ ) of SST ( $\Delta$ SST), SSS ( $\Delta$ SSS),  $\Delta f$ CO<sub>2</sub> ( $\Delta \Delta f$ CO<sub>2</sub>), FCO<sub>2</sub> ( $\Delta F$ CO<sub>2</sub>) between the monthly averaged estimations of the Takahashi's climatology (Takahashi et al., 2009) and these in situ measurements in the ocean waters during the FICARAM cruises ( $X^{\text{FICARAM}} - X^{\text{TCO9}}$ ).  $\Delta \Delta f$ CO<sub>2</sub> was estimated correcting  $\Delta \Delta f$ CO<sub>2</sub> from  $\Delta$ SST values and assuming the theoretical temperature control described by Takahashi et al. (1993). To compare the climatological FCO<sub>2</sub> values to our estimations, we multiplied  $\Delta \Delta f$ CO<sub>2</sub> with climatological k and S according to Eq. 3.

Region	Boreal	$\Delta SST$	$\Delta SSS$	$\Delta \Delta fCO_2'$	$\Delta\Delta fCO_2$	$\Delta FCO_2$
	Season	°C		μatm	µatm	$ m molm^{-2}yr^{-1}$
ENAS	spring	$0.2 \pm 0.4$	$0.0\pm0.2$	$-10\pm 6$	$-13\pm7$	$-0.8\pm0.5$
39–27° N	autumn	$0.6\pm0.4$	$0.1\pm0.1$	$12\pm7$	$3\pm9$	$0.2 \pm 0.4$
CC	spring	$0.1\pm0.3$	$0.0\pm0.2$	$-5\pm7$	$-7\pm9$	$-0.4 \pm 0.5$
27–16° N	autumn	$0.6\pm0.8$	$0.1\pm0.2$	$10\pm12$	$3 \pm 11$	$0.1 \pm 0.6$
NEC	spring	$0.6\pm0.4$	$-0.1\pm0.1$	$-13\pm12$	$-19\pm11$	$-1.2\pm0.7$
16–8° N	autumn	$0.5\pm0.5$	$-0.1\pm0.3$	$-5 \pm 12$	$-13 \pm 12$	$-0.6\pm0.6$
NECC	spring	$0.5\pm0.2$	$-0.3\pm0.2$	$-9\pm13$	$-16\pm13$	$-0.8\pm0.6$
$8^{\circ}-1^{\circ} N$	autumn	$0.3\pm0.5$	$-0.5\pm0.4$	$-6\pm 12$	$-10\pm17$	$-0.4\pm0.5$
SEC	spring	$0.2\pm0.2$	$0.0\pm0.2$	$2\pm 8$	$-6\pm9$	$-0.3 \pm 0.4$
1° N–15° S	autumn	$0.1 \pm 0.4$	$-0.1\pm0.2$	$-2\pm9$	$0\pm 13$	$0.0\pm0.9$
STG	spring	$1.0\pm0.7$	$0.3\pm0.3$	$6\pm17$	$-10\pm11$	$-0.4 \pm 0.5$
15–31° S	autumn	$0.5\pm0.6$	$0.1\pm0.2$	$2\pm15$	$-4 \pm 15$	$-0.3\pm0.8$
SAS	spring	$1.0\pm0.6$	$0.0\pm0.3$	$-1\pm19$	$-16\pm16$	$-1.1\pm1.2$
31–40° S	autumn	$-0.2\pm0.6$	$0.4 \pm 0.3$	$-15\pm10$	$-12\pm9$	$-1.0\pm0.8$
SAC	spring	$-1.8\pm1.9$	$0.0\pm0.1$	$-5\pm16$	$23\pm40$	$2.0 \pm 3.4$
40–51° S	autumn	$-0.9\pm1.3$	$-0.2\pm0.2$	$-20\pm26$	$-13 \pm 34$	$-1.1 \pm 3.0$
FC	spring	$-0.3 \pm 0.5$	$-0.1 \pm 0.1$	$8\pm27$	$14\pm32$	$1.7 \pm 3.9$
51–56° S	autumn	$-0.1\pm0.6$	$-0.1 \pm 0.3$	$-22\pm35$	$-21 \pm 43$	$-2.5 \pm 5.3$
DP						
56–66° N	autumn	$-0.9\pm0.7$	$-0.1\pm0.2$	$-27\pm19$	$-13\pm22$	$-1.5\pm2.2$

results support the consistency between both datasets and the validity of the  $CO_2$  climatology along the Atlantic Ocean during spring and autumn seasons. However the comparison at regional scale showed some offsets that are detailed below.

The oceanic waters of the ENAS region in April showed significant intensification of  $13 \pm 7 \mu atm$  in the CO<sub>2</sub> undersaturation of the interpolated values from TCO9 (Table 4). This difference under average conditions of solubility and transfer velocity reported by Takahashi et al. (2009) would produce an offset in the CO<sub>2</sub> uptake of  $0.8 \pm 0.5 \text{ mol m}^{-2} \text{ yr}^{-1}$ . Contrary to these disagreements in  $\Delta f \text{CO}_2$  and  $F \text{CO}_2$  in spring, the near equilibrium status of these waters in autumn was closely reproduced by both databases showing a difference of  $3 \pm 9 \mu \text{atm}$ .  $\Delta \Delta f \text{CO}_2$  values in the CC province also pointed out the agreement in the  $\Delta f \text{CO}_2$  observations (Table 4) in spite of the complex hydrography related to the intense upwelling events

that characterize this region (Mittelstaedt, 1991). In this sense, long-term changes in the WS indicated a relaxation of the coastal upwelling (Roy and Reason, 2001) of  $-0.30 \pm 0.07 \,\mathrm{m \, s^{-1} \, yr^{-1}}$  in spring that it was even reproduced in a lesser extent in autumn. The direct WS-'  $f CO_2^{sw}$ relationship (Table 3) suggests an increase of the stratification and so, a reduction of the mixing processes with subsurface CO<sub>2</sub> rich waters. However any significant change directly related to upwelling processes was observed in other variables (Fig. 4b). As a result, the chl a signal was unlikely to have been detected in surface ocean waters because of its confinement to the coast at these latitudes (Arístegui et al., 2009) associated to limitation in the surface nitrate concentration (Lauthuilière et al., 2008). Nevertheless the chl a signal associated with the intense seasonal upwelling in the NEC province and to the south of Cape Blanc (10-19° N), extends to open ocean regions from February to May (Aristegui et al., 2009). The remotely retrieved observations of chl a in this region showed a long-term spring decrease of  $-0.03 \pm 0.01$  mg m<sup>-3</sup> yr<sup>-1</sup> as was reported by Gregg et al. (2005). This finding implies a net reduction of the biological CO<sub>2</sub> uptake (Table 3) during the spring cruises and also seems to explain the general year-to-year decrease of CO<sub>2</sub> saturation (Fig. 4b, c). Nevertheless and in spite of this  $\Delta f CO_2$  increase, spring  $\Delta f CO_2$  measurements that were mainly controlled by SST exceeded the climatological undersaturation close equilibrium status with the atmosphere (Takahashi et al., 2009). SSS changes controlled the  $\Delta f CO_2$ distribution in autumn in which  $\Delta \Delta f CO_2$  reached an offset of  $13 \pm 12\mu$ atm leading the slight CO<sub>2</sub> outgassing of TCO<sub>9</sub> (Takahashi et al., 2009) to null role as sink or source (Table 2). Therefore the long-term changes of the subtropical waters of the North Atlantic Ocean in spite of not being statistically significant pointed out a reduction in outgassing (Fig. 4c) as was observed in the ESTOC site (Santana-Casiano et al., 2007).

In the light of these results, the analysis of the FICARAM dataset supports recent work reporting the weakening of the upwelling events in parallel to the decrease of primary production in the Canary upwelling system (Santos et al., 2005; Chavez and Messié, 2009; Pérez et al., 2010). The relaxation of the Atlantic trade winds is directly linked to the decrease of the pressure gradient between the Azores High and the Icelandic Low. This scenario is described by the negative index of the NAO (Hurrell et al., 1995) that prevailed during the sampling period of FICARAM cruises. Apart from explaining the observed WS declination in this region of the North Atlantic, this large-scale climatic phenomenon is also related to the northward displacement of the waters from Azores current into the temperate regions (Flatau et al., 2003; Siedler et al., 2005; Häkkinen and Rhines, 2009). The northward advection of these waters is linked to several changes of the different biogeochemical variables in the North Atlantic Ocean (Marshall et al., 2001). Amongst others, warming of surface waters in the eastern tropical and subtropical gyre was associated with the NAO declination (Marshall et al., 2001; Santana-Casiano et al., 2007). Under this scenario,  $\Delta f CO_2$  would also increase reducing the ocean uptake of atmospheric CO<sub>2</sub> (Patra et al., 2005; Schuster et al., 2009), such as it was observed in the North Atlantic waters (Schuster and Watson, 2007; Thomas et al., 2008; Herbaut and Houssais, 2009). The analysis of the FICARAM cruises mostly reproduced these changes over decadal scale showing a faster increase of the  $f CO_2^{sw}$  in relation to the trend of atmospheric CO<sub>2</sub>. Even the time delay beyond its maximum period of influence from December to March (Osborn, 2007), that is, during the spring cruises, linked to impact on physical and biological processes (Patra et al., 2005) affected autumn  $FCO_2$  as well. However the long-term analysis did not show a SSS declination related to the northward advection of less saline waters (Santana-Casiano et al., 2007). Notwithstanding the direct influence of the NAO index on the water mass distribution affecting  $f CO_2^{sw}$  in the region (Lauvset et al., 2010), the presence of upwelled waters makes it difficult to interpret these results (Fig. 2a, b). The  $\Delta\Delta f CO_2$  estimations in these regions should predominantly be positives as result of the comparison between  $\Delta f CO_2$  of a prevailing negative NAO period and average  $\Delta f CO_2$  values from different NAO scenarios gathered in TC09. Nevertheless the reduced number of the FICARAM cruises in these complex regions did not appropriately reproduce the monthly averages of the coarse grid of TC09 (Takahashi et al., 2009). Disagreements were especially notable in spring in which  $\Delta f CO_2$ reaches a short minimum as result of the single spring bloom (Santana-Casiano et al., 2007).

The tropical waters of the eastward flowing NECC region also showed lower  $\Delta f CO_2$  values and consequently, a reduction of the CO<sub>2</sub> outgassing, during the FICARAM cruises in both seasons. In spite of these differences, significant offset of  $-16 \pm 13$  µatm was only found in spring and reduced the role of these waters as CO<sub>2</sub> source in TCO9 by  $0.8 \pm 0.6 \text{ mol m}^{-2} \text{ yr}^{-1}$ . The supersaturation in autumn was also underestimated, namely, by  $-10 \pm 17 \,\mu atm$ , yielding a difference of  $-0.4 \pm 0.5 \text{ mol m}^{-2} \text{ yr}^{-1}$ . Both  $\Delta f \text{CO}_2$ disagreements coincided with important SSS differences of  $0.5 \pm 0.4$  and  $0.3 \pm 0.2$  in spring and autumn, respectively. The effect of  $\triangle$ SSS on the CO<sub>2</sub> solubility and carbonic acid dissociation constants (Takahashi et al., 1993) was not considered in the estimation of  $\Delta \Delta f CO_2$  as it was done for  $\Delta$ SST. Nevertheless, this correction would be inversely proportional to the  $\triangle$ SSS and it would only increase the observed disagreement by around 1 µatm. However the estimation of empirical relationships that correctly fitted in  $f CO_2^{sw}$ distribution in both seasons (Table 3) has identified the role of the SSS changes as an important driver of  $\Delta f CO_2$  variability. The impact of the SSS changes on the  $\Delta f CO_2$  distribution was especially outstanding in autumn, when they explained 79% of the variability of the estimated ' $f CO_2^{sw}$  values with a coefficient of  $17.3 \pm 0.3 \,\mu$ atm per SSS unit (Table 3). Therefore less saline waters attributed to the discharges of the Orinoco, Parana and Amazon rivers (Müller-Karger et al., 1988; Ternon et al., 2000; Wanninkhof et al., 2007) and the intensification of eastward currents (Richardson and McKee, 1984) seemed to strongly lead the  $\Delta f CO_2$  changes, especially in autumn. Continental inputs fertilizing the surface tropical waters and stimulating the biological CO2 drawdown would explain the positive estimated ' $f CO_2^{sw} - SSS$ relationships, that is, the observed direct control on  $\Delta f CO_2$ (Lefèvre et al., 1998; Subramanian et al., 2008). Reinforcing this supposition, SSS decreases during the autumn cruises (Fig. 4) were observed in parallel to a significant reduction of CO<sub>2</sub> saturation and outgassing in  $-3.5 \,\mu atm \, yr^{-1}$ and  $-0.09 \pm 0.03 \text{ mol m}^{-2} \text{ yr}^{-2}$ , respectively. The interannual fluctuations of the discharges of Orinoco, Parana and Amazon Rivers showed different relationships with largescale alterations of the atmospheric pressure. In any case, Orinoco shows some relationship with these climatologic indicators (Hastenrath, 1990) while Parana discharges that showed stationary positive correlations with NAO are intermittently influenced by ENSO (Labat et al., 2005). On the other hand, the discharges of the Amazon River show an important and nearly permanent inverse correlation with the ENSO (Zeng, 1999; Labat et al., 2005). In spite of the key control that plays these climatic indexes, the long-term SSS decrease and its influence on the  $\Delta f CO_2$  changes in NECC are difficult to interpret from NAO and ENSO considering the prevailing negative NAO period and a predominant positive ENSO scenario that dominated the FICARAM period.

The SEC region that closely interacts with the NECC region through the meridional displacements of the InterTropical Convergence Zone was characterized by higher  $\Delta f CO_2$ (Table 2) than the tropical waters further north (Govet et al., 1998; Takahashi et al., 2009). The strong CO<sub>2</sub> supersaturation of this region was markedly similar to both FICARAM and TC09 datasets (Table 3).  $\Delta f CO_2$  and  $F CO_2$ in autumn showed slight underestimations of  $-6 \pm 9 \mu atm$ and  $-0.3 \pm 0.4 \text{ mol m}^{-2} \text{ yr}^{-1}$ , respectively, while  $\Delta \Delta f CO_2$ in spring was negligible ( $0 \pm 13 \,\mu atm$ ) representing  $\Delta f CO_2$ values of  $0.0 \pm 0.9 \text{ mol m}^{-2} \text{ yr}^{-1}$ . The spring agreements in the equatorial upwelling system that were the highest observed along the Atlantic Ocean were observed in parallel to significant changes at long-term scale. So, trade equatorial winds in the western basin of the South Atlantic showed a relaxation in parallel to the warming of the surface waters (Fig. 4e). The WS and SST anomalies in the tropical Atlantic over interannual scales were significantly related to the ENSO phenomenon (Enfield and Mayer, 1997; Latif and Grötzner, 2000). Consequently, positive SST anomalies prevail over the western equatorial Atlantic during the warm ENSO events as result of a reduction in the speed of trade winds. These long-term drifts seem to be connected to the response of the decreasing upwelling intensity that directly affects to the thermocline depth (Grodsky et al., 2008). Furthermore the teleconnection between Pacific and Atlantic Oceans is clearly evident during the boreal spring (Enfield and Mayer, 1997) as evident in the FICARAM cruises as well.

The seasonal CO<sub>2</sub> outgassing and absorption of the STG region in spring and autumn (Takahashi et al., 2009), respectively, were correctly reproduced by the FICARAM cruises (Table 3). Nevertheless poor agreements were observed during spring in spite of most values of Table 4 showing consistent results. So, FICARAM dataset roughly pointed out 23 °C (Fig. 2, 3; Table 2) determined by Ito et al. (2005) as the boundary between if the oceanic waters of the STG region acted as sink or source of CO<sub>2</sub> for the atmosphere. The SST changes yielded a considerable effect on  $f CO_2^{sw}$  (Ito et al., 2005) with a relative importance of SSS and chl *a* in spring and autumn, respectively (Table 3).

Nevertheless SAS region that acted as a strong sink of atmospheric CO<sub>2</sub> (Bianchi et al., 2009) showed significant offsets in October with values of  $\Delta\Delta f CO_2$  and  $\Delta f CO_2$  of  $-12 \pm 9 \,\mu$ atm and  $-1.0 \pm 0.8 \,\mathrm{mol} \,\mathrm{m}^{-2} \,\mathrm{yr}^{-1}$ , respectively

(Table 4). Strong SSS anomalies of  $0.4 \pm 0.3$  were found at the same month, which coincides with the most intense discharges of River Plate (Guerrero et al., 1997). Similar increases of  $-1.1 \pm 1.2 \text{ mol m}^{-2} \text{ yr}^{-1}$  were observed during boreal spring with no average SSS differences. Results of the empirical estimation of the biochemical forcing showed a minimum influence of SSS on the  $\Delta f CO_2$  variability in both seasons. The  $\Delta f CO_2$  distribution was mostly controlled by the SST variability, especially in March, when it explained 85% of ' $f CO_2^{sw}$  variability (Table 3). The  $f CO_2^{sw}$  distribution in November was controlled by SST with WS and chl a variables even though only 37% of  $f CO_2^{sw}$  changes were explained by these variables. So, the notable weight of the Plata River in the SAC region in autumn (Gordon, 1989) affecting the nutrient inputs (Bakun and Parrish, 1991) and controlling the production of chl a in the Patagoninan Sea (Froneman et al., 1999) was not properly accounted for using this simplistic approach.

The southern surface waters of the Patagonian Sea were systematically colder than the reported by TC09 reaching the lowest  $\triangle$ SST of  $-1.8 \pm 1.9$  °C in SAC region during March cruises. The  $\Delta \Delta f CO_2$  and  $\Delta f CO_2$  values of these waters in March showed notable supersaturation of  $23 \pm 40 \,\mu$ atm of FICARAM dataset that underestimated the climatological CO<sub>2</sub> uptake (Takahashi et al., 2009) in  $2.0 \pm 3.4 \text{ mol m}^{-2} \text{ yr}^{-1}$  (Table 4). Conversely the undersaturation of these waters was overestimated by  $-13 \pm 34 \,\mu atm$ in October. The differences between in situ  $f CO_2^{sw}$  and values from empirical relationships were also maximum in the Patagonian Sea, with differences of 31.9 µatm being found in SAC waters during the autumn cruises (Table 3). Apart from the low number of measurements used to characterize these regions in both dataset, these disagreements reflect the complex hydrography and the heterogeneous  $f \operatorname{CO}_2^{sw}$  distribution (Bianchi et al., 2005). Nevertheless some typical features of these waters were correctly described such as the notable outflow of the continental ice melting in the Pacific coast of Tierra de Fuego through the Magellan Strait (Fig. 2b, c; Piola and Rivas, 1997). These freshwater inputs enrich the surface nutrient concentration supporting the spring phytoplankton bloom and resulting in the observed CO<sub>2</sub> undersaturation of the coastal and ocean waters (Table 2; Romero et al., 2006). Nevertheless ' $fCO_2$ -chl a relationships of the FC region far from representing phytoplankton CO<sub>2</sub> consumption showed similar positive values that were attributed to CO<sub>2</sub> inputs from continental inputs or remineralization processes. The non-synoptic sampling strategies followed in the FICARAM project could cause positive coefficients during the monitoring of senescent phytoplankton community. In relation to the long-term trends observed in these waters, the atmospheric pressure changes of the Southern Ocean represented by SAM could explain some of the observed interannual drifts. SAM variability that is related the Southern Ocean circulation through meridional shifts in the wind patterns (Hartamann and Lo; 1998) significantly affects biogeochemical cycling and  $FCO_2$  (Lovendrusky et al., 2007) of the Patagonian Sea. Therefore the significant WS weakness reported at these latitudes (Fig. 4g, h) could directly be associated with positive SAM values, which showed a slight increase during the FICARAM period. Warm SST anomalies and an increase of CO<sub>2</sub> outgassing that are also driven by positive phases of the SAM (Lovendrusky et al., 2007) could approximately be noticed from year 2005 as well (Fig. 4 g, h and i).

The DP region was crossed during two FICARAM cruises that only gathered underway measurements in November. The average  $\Delta f CO_2$  of  $-20 \pm 11 \,\mu atm$  measured in the ocean waters (Table 2) described this branch of the Southern Ocean as a sink of atmospheric  $CO_2$  (Metzl et al., 1999). This value is  $13 \pm 22 \,\mu$ atm lower than the climatological  $\Delta f CO_2$  (Takahashi et al., 2009) which showed an average outgassing of 10 µatm for this month. The FICARAM observations that came to findings of the different approaches (Metzl et al., 1999; Metzl, 2004; Gurney et al., 2002; Roy et al., 2003; McNeil et al., 2007) confirmed in the role of these waters as a sink of atmospheric CO<sub>2</sub> that was reported by Gruber et al. (2009). The CO<sub>2</sub> undersaturation of these waters showed a notable interannual variability as was found by Metzl (2004). The found  $\Delta f CO_2$  shift (Fig. 3b) between both Novembers can be explained by changes in thermohaline properties (Fig. 2b, d). So, colder and saltier waters in 2007 pointed to an intensification of the upwelling of North Atlantic Deep Water (Nowlin and Klink and, 1986) that led  $\Delta f CO_2$  values close to equilibrium status (Fig. 3b). On the other hand, warmer and less saline waters in 2008 showed a southward growing undersaturation that caused a CO2 uptake of  $-1.8 \pm 1.2 \text{ mol m}^{-2} \text{ yr}^{-1}$ . This intense CO<sub>2</sub> absorption, which was associated with photosynthetic activity of  $0.17 \pm 0.01$  mg m-3, was also linked to the entrance of deep waters that increased the surface iron concentration (Metzl et al., 1991; Legendre et al., 1992; Poisson et al., 1994; Arrigo et al., 1997). This is somewhat lower phytoplanktonic community activity than reported during the spring bloom in the subAntarctic coastal area (Perissinotto et al., 2000; Blain et al., 2001; Delille et al., 2007). South of the Continental Water Boundary ( $\sim 62^{\circ}$  S; Fig. 2d) and where lowest  $\Delta f CO_2$ values were found, the role of surface waters change from a source to a sink of atmospheric CO<sub>2</sub>. Consequently  $\Delta f CO_2$ of shelf waters of the Livingston Island showed a coastward increase in parallel to SSS that reached 27 µatm causing an outgassing of  $0.8 \text{ mol m}^{-2} \text{ yr}^{-1}$  (Fig. 3b, d).

### 5 Summary

The FICARAM programme has proved to be a new source of information about the changing air-se  $CO_2$  fluxes in the Atlantic Ocean. Moveover FICARAM cruises represented a unique opportunity to analyze from a quasi-synoptic point of view underway  $fCO_2^{sw}$  measurements in spring and autumn along an ample array of hydrographic regions of both Hemispheres. These measurements of the FICARAM cruises, that were independent of the surface ocean CO<sub>2</sub> atlas recently constructed by Takahashi et al. (2009), mostly reproduced the climatological estimations showing a mean  $\Delta f CO_2$  difference of  $-3 \pm 18 \mu \text{atm}$ . This reduction in the CO<sub>2</sub> saturation of the surface waters represented an increase of  $0.02 \pm 0.14 \text{ mol m}^{-2} \text{ yr}^{-1}$  in the ocean uptake of atmospheric CO<sub>2</sub>. Moreover  $f CO_2^{\text{sw}}$  measurements have allowed the detection of some changes in the long-term trends of the fluxes in some regions of the Atlantic Ocean. Shelf regions were also sampled along the coasts of Africa and South America. In general terms, the shelf waters repeated the behave of the adjacent waters even though emphasizing the observed results in both spring and autumn. The most remarkable results obtained are:

- 1. The Northern Subtropical Gyre acted as a sink of atmospheric CO<sub>2</sub> during the successive spring seasons  $(-1.8 \pm 1.2 \text{ mol m}^{-2} \text{ yr}^{-1})$  and as a source during autumn  $(0.2 \pm 0.4 \text{ mol m}^{-2} \text{ yr}^{-1})$ . Similarly, the subtropical waters of the Southern Hemisphere absorbed CO<sub>2</sub> under spring conditions  $(-0.2 \pm 0.7 \text{ mol m}^{-2})$  $yr^{-1}$ ), while CO<sub>2</sub> outgasing occurred during autumn  $(0.6 \pm 0.6 \text{ mol m}^{-2} \text{ yr}^{-1})$ . The seasonal distribution of  $f CO_2^{sw}$  in these latitudes was mainly determined by changes in SST that explained more than 80% of the  $f CO_2^{sw}$  variability, according to the proposed algorithm. Negative NAO scenario that prevailed during the sampling period of FICARAM cruises was linked to longterm declination of WS  $(0.30 \pm 0.07 \text{ m s}^{-1} \text{ y}^{-1})$  and chl  $a (0.03 \pm 0.01 \text{ mg m}^{-3} \text{ y}^{-1})$  that reinforce works reporting the weakening of the upwelling events in the Canary upwelling system (Santos et al., 2005; Chavez and Messié, 2009; Pérez et al., 2010). Under this pressure pattern of the North Atlantic Ocean, FICARAM measurements roughly pointed out the expected warming and the reduction of the ocean uptake of atmospheric  $CO_2$ .
- 2. Tropical waters were virtually in equilibrium with the atmosphere during spring and autumn, which yielded triffing air-sea CO<sub>2</sub> fluxes, especially in the NECC region. The analysed property distributions in the latter province revealed a significant long-term decrease of SSS  $(-0.16 \pm 0.01 \text{ yr}^{-1})$  during the successive autumn cruises. At the same time, outstanding  $\Delta f CO_2$  reduction  $(-3.5 \pm 0.9 \,\mu \text{atm yr}^{-1})$  and a rise of oceanic CO<sub>2</sub> uptake  $(-0.09 \pm 0.03 \text{ mol m}^{-2} \text{ yr}^{-1})$ . These strong SSS changes produced by the Amazon River outflows accounted for 79% of the observed  $f CO_2^{\text{sw}}$  variability in autumn and 49% in spring, providing uplift to the role of freshwater discharges in the uptake of CO<sub>2</sub>.
- 3. To the south of the equator, the tropical waters of the equatorial upwelling system were highly supersaturated, exceeding the atmospheric CO<sub>2</sub> concentration

in spring and autumn by  $24 \pm 12$  and  $30 \pm 11 \mu atm$ , respectively. These CO<sub>2</sub>supersaturations represented a spring – autumn range of CO<sub>2</sub> outgassing that eventually reached southern latitudes in autumn of  $0.7 \pm 0.5$  and  $1.0 \pm 0.7 \text{ mol m}^{-2} \text{ yr}^{-1}$  in spring. An interannual surface warming of  $0.11 \pm 0.03 \text{ }^{\circ}\text{C yr}^{-1}$  and a WS decrease of  $-0.58 \pm 0.14 \text{ m s}^{-1} \text{ yr}^{-1}$  characterized these waters during the successive spring cruises, which suggest the weakening of upwelling (Grodsky et al., 2008) that was directely associated with the warm ENSO events that dominated the FICARAM period (Enfield and Mayer, 1997; Latif and Grötzner, 2000).

- 4. The majority of provinces in the Patagonian Sea were systematically colder than the reported by Takahashi et al. (2009) and behaved as an intense sink of CO<sub>2</sub> in both southward or northward cruises. In particular, oceanic waters of the SAC province were the strongest CO<sub>2</sub> sink registered by the FICARAM cruises, namely,  $-5.4 \pm 3.6 \text{ mol m}^{-2} \text{ yr}^{-1}$  in November. The heterogeneous distributions of  $\Delta f \text{CO}_2$  and  $F \text{CO}_2$  in the Patagonian shelf were not well explained by either SST, SSS or chl *a*. The complex hydrography (Bianchi et al., 2005) and the scarce cruises held in this region yielded the worst adjustment of the  $f \text{CO}_2^{\text{sw}}$  observations.
- 5. The ocean branch of the Antarctic waters sampled in the Drake Passage in November were CO<sub>2</sub> undersaturated in  $-20 \pm 11 \,\mu$ atm. These oceanic waters displayed an average uptake rate of  $-1.1 \pm 0.9 \,\mathrm{mol} \,\mathrm{m}^{-2} \,\mathrm{yr}^{-1}$  that were characterized by a notable change between the November of 2007 and the November 2008. On the other hand, the distal shelf of the Livingston Island acted as a slight source of CO<sub>2</sub> to the atmosphere  $(0.1 \pm 0.3 \,\mathrm{mol} \,\mathrm{m}^{-2} \,\mathrm{yr}^{-1})$ .

Acknowledgements. We would like to extend our gratitude to the Captains and crew of B/O Hespérides and B/O Las Palmas for their hospitality and essential help, and to the UTM team for their logistic support. We are especially grateful to Iago Rodicio and Marcos Villafn who occupied of the IT support throughout the nine years of FICARAM cruises. We also thank to Adrian Callaghan and Jonathan Bares for substantially improving the writing style of the manuscript. Three anonymous reviewers provided valuable comments and suggestions to a first version of the manuscript. This study was developed and funded by the European Commission within the 6th Framework Programme (EU FP6 CARBOOCEAN Integrated Project, Contract no. 511176), the Spanish research project FICARAM (CICYT. REN 2000-2467-E and 2001-4839-E), Ministerio de Ciencia e Innovación (CTM2006–27116–E/MAR) and Xunta de Galicia (PGIDIT05PXIC40203PM).

Edited by: A. V. Borges

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