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Air–sea CO_2 flux variability in frontal regions of the Southern Ocean from CARbon Interface OCean Atmosphere drifters

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Web Appendix 1. Calibration of CARIOCA systems and comparison with in situ measurements

Laboratory calibration of the CARIOCA spectrophotometers

Calibration of the spectrophotometer system is performed in the laboratory a few months before deployment. The standard deviation of the difference obtained in the laboratory between CARIOCA fCO_2 (fugacity of CO_2 in seawater) and classical measurement using the equilibrator-infrared absorption system, σcal, is reported in (Table A1.1). Lower standard deviations after 2003 are due to improvements in temperature controls of infrared and spectrophotometer systems. These laboratory calibrations indicate an accuracy of CARIOCA fCO_2 measurements of 0.3 Pa or better.

Comparison of CARIOCA fCO_2 with in situ measurements

Whenever possible, additional checks of CARIOCA measurements were performed at sea immediately after CARIOCA deployments. When fCO_2 was measured on board ship, we compared CARIOCA fCO_2 with ship fCO_2 positioned as close as possible to the buoys. Where two CARIOCA buoys were deployed during the same ship station, we compared the fCO_2 measured by the two buoys. This exercise is quite complex as CARIOCA buoys take reliable fCO_2 measurements only several hours after their deployment, so that the ship and the buoy rarely measure fCO_2 at the same place and time.

In 2002, since the two buoys were deployed at the same place, it is possible to compare their measurements just after their deployment, when they were close in place and time (Table A1.2). ΔfCO_2 is quite consistent with the results obtained during laboratory calibration of the buoys. We also seek to compare CARIOCA fCO_2 with that measured on board ship during the OISO8 campaign (N. Metzl pers. comm.). However, the buoys were deployed in a very variable area, close to the SAF: they were deployed on 12 Jan at 21:30 h, but took reliable fCO_2 measurements only after 13 Jan at 18:00 h. During that period of time, the buoy No. 2 recorded SST (sea surface temperature) varying from 11.43°C to 12.10°C and SSS (sea surface salinity) varying from 34.12 to 34.10, which meant that it was impossible to compare ship and buoy measurements directly. Instead, by comparing SSS–SST diagrams from the ship and from the buoy No. 2 during the week after deployment, we concluded that there was a difference in fCO_2 measured in the same range of SST and SSS of < -0.27 Pa.

In 2003, buoys No. 4 and No. 5 were deployed simultaneously on 30 Jan 2003 and stayed very close together until 01 Feb 11:00 h. In Table A1.3, we report the mean differences when both buoys performed reliable fCO_2 measurements (from 31 Jan 01:00 h). ΔfCO_2 is consistent with the laboratory calibration of the buoys (accuracies of 0.15 and 0.2 Pa); nevertheless, for the data analysis presented in this paper, we have corrected for the mean bias, by decreasing the fCO_2 of buoy No. 5 by 0.15 Pa and by increasing the fCO_2 of buoy No. 4 by 0.15 Pa. Buoys were deployed during the OISO 10 cruise. From pCO_2 measured during OISO 10 (N. Metzl pers. comm.), we calculate the ship fCO_2, which we compare to the CARIOCA measurements (Table A1.4). Given the amount of time separating the ship and CARIOCA measurements, the comparison is very close.

In 2004, the two buoys were launched from the *R/V Tangaroa* on 24 Mar at 20:00 h (buoy No. 7) and 11 Apr at 20:00 h (buoy No. 6). Sampling depth on the *R/V Tangaroa* is 4 m, and fCO_2 accuracy is estimated ± 0.3 Pa (K. Currie pers. comm.).

Table A1.1. Laboratory calibration of CARIOCA buoys.

Year	Buoy No.	σcal (Pa)
2001	1	0.31
2002	2	0.23
2002	3	0.32
2003	4	0.15
2003	5	0.20
2004	6	0.12
2004	7	0.12
2005	8	0.17
2006	9	0.27

Table A1.2. Comparison of 2002 fCO_2 (buoys No. 2 and No. 3). Δx, ΔSST, and ΔfCO_2 are, respectively, the distance between the two buoys, the differences in SST and fCO_2, averaged during the period.

Date	Time (h)	Δx (km)	ΔSST (°C)	ΔfCO_2 (Pa)
13 Jan	19:00–22:00	6.7	0.02	−0.058
14 Jan	12:00–18:00	3.8	0.02	0.011

Table A1.3. Comparison of 2003 measurements (buoys No. 5 minus No. 4). Δx, ΔSST, and ΔfCO_2 are, respectively, the distance between the two buoys, the differences in SST and fCO_2, averaged over the period.

Date time (h) period	Δx (km)	ΔSST (°C)	ΔSSS	ΔfCO_2 (Pa)
31 Jan 01:00–01 Feb 11:00	<2	−0.002	0.006	0.279

Table A1.4. Comparison of CARIOCA No. 4 and No. 5 with *Tangaroa* ship measurements performed on 30 Jan between 15:00 h and 15:15 h. Δx, Δt, ΔSST, and ΔfCO_2 are, respectively, the distance in space and time between the ship and the buoy, the differences (ship minus CARIOCA) in SST and in fCO_2 averaged over the period.

	Date	Time (h)	Δx (km)	Δt (h)	ΔSST (°C)	ΔfCO_2 (Pa)
Carioca No. 4	30 Jan	23:00–05:00	<3	12	−0.007	0
Carioca No. 5	31 Jan	01:00–05:00	<3	13	0.003	−0.12

Table A1.5. Comparison of CARIOCA No. 7 with *Tangaroa* ship measurements. Δx, Δt, ΔSST, ΔSSS, and ΔfCO_2 are, respectively, the distance in space and time between the ship and the buoy, the differences (ship minus CARIOCA) in SST, in SSS, and in fCO_2.

	Date	Time (h)	Δx (km)	Δt (h)	ΔSST (°C)	ΔSSS	ΔfCO_2 (Pa)
CARIOCA & ship	25 Mar	17:00–24:00	3	0	0.01	0.00	0.32
Ship	10 Apr	02:25					
CARIOCA	10 Apr	20:00	1.5	18	0.20	0.02	−1.09

Table A1.6. Comparison of CARIOCA No. 6 with *Tangaroa* ship measurements. Δx, Δt, ΔSST, ΔSSS, and ΔfCO are, respectively, the distance in space and time between the ship and the buoy, the differences (ship minus CARIOCA) in SST, in SSS, and in fCO_2.

	Date	Time (h)	Δx (km)	Δt (h)	ΔSST (°C)	ΔSSS	ΔfCO_2 (Pa)
Ship	11 Apr	21:00					
Carioca	12 Apr	11:00	<1	14	0.05	0.01	0.73

In Tables A1.5 and A1.6, we report differences between the ship and the buoy when they were the closest in time or place.

It is important to note that ship fCO_2 decreases by 0.6 Pa in 2.5 h, just after the departure of the ship from the station where CARIOCA No. 6 was deployed, while SSS remains stable so that difference in fCO_2 reported in Table A1.6 could be due to temporal variation.

The three situations we considered in order to compare ship and 2004 buoy measurements do not allow us to draw any conclusions, because we have significantly different results both for the ship and buoy No. 7 pair over a time period of 16 d and for the ship and buoy No. 6 pair, because ship measurements were variable over a few hours.

The natural oceanic mesoscale variability is certainly a candidate that might explain the observed differences. These may relate to differences in the patterns of turbulence and breaking waves around the ship or around the drifters, as well as to differences in the respective sampling depths.

In conclusion, careful analysis of the SAGE field data does not allow us to establish whether there is a difference between the fCO_2 measurements of the ship and the drifters, and it is consistent with accuracy of CARIOCA fCO_2 measurements of 0.3 Pa.

Relative precision of CARIOCA fCO_2

Laboratory tests with CARIOCA technology have shown a reproducibility of ±0.05 Pa over short time periods at constant temperature (Lefèvre et al. 1993). At sea, in the tropical Atlantic Ocean, small variations between consecutive fCO_2 measurements and detection of diurnal fCO_2 cycles linked to SST diurnal cycles support the high precision of the instrument (Bakker et al. 2001). In the Southern Ocean, the amplitude of diurnal cycles is much smaller so this exercise is trickier. Nevertheless, an example of diurnal fCO_2 cycle associated with diurnal SST cycle recorded by one of the 2003 buoys, used in this paper is shown in Fig. A1.1. Jumps between two consecutive measurements are always <0.1 Pa. Differences with respect to fCO_2 calculated from a DIC constant over this time period show a very similar diurnal cycle, indicating that SST is the main driver for the observed variability. The differences between measured and calculated fCO_2 are always between ±0.1 Pa. Given that this observation also includes natural variability at sea (the diurnal cycle of SST is not purely sinusoidal), it supports a relative precision for CARIOCA fCO_2 of 0.1 Pa.

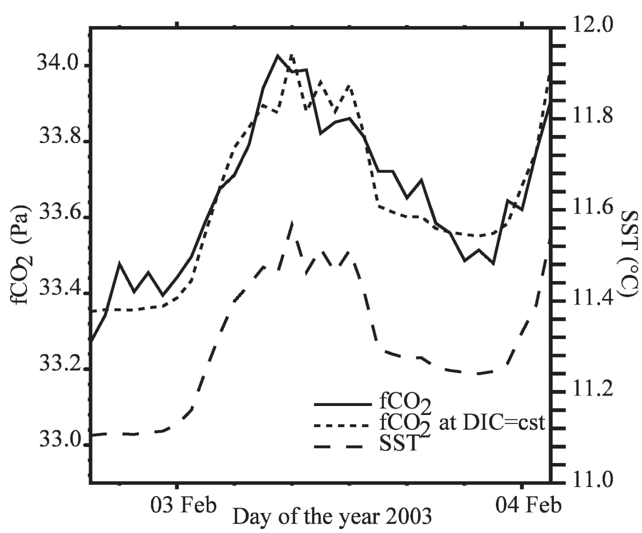

Fig. A1.1. SST and fCO_2 measured between 03 and 04 Feb 2003 by buoy No. 4. The diurnal fCO_2 variation can be explained by the diurnal cycle of the SST as shown by the fCO_2 calculated from a constant DIC (=2067.7 μmol kg^{-1}). Differences between calculated and measured fCO_2 come from both the relative precision of fCO_2 and the natural variability.