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## Variations of the partial pressure of CO<sub>2</sub> in the surface waters of the Northwest African upwelling system in summer 1999.

Marta Álvarez

Instituto de Investigaciones Marinas, CSIC. C/ Eduardo Cabello, Nº 6, 36200. Vigo, SPAIN

The Northwestern African upwelling region is typical in terms of the presence of filaments (Van Camp *et al.*, 1991). Its specific characteristic relates with the presence of the Canary Islands, which provide a major source of mesoscale activity (Arístegui *et al.*, 1994; Arístegui *et al.*, 1997). During August 1999 the FAX cruise was carried out on board the R/V Hespérides and sampled waters off the Northwest African coast, offshore Cape Juby.

The FAX cruise had as an overall objective to estimate the fluxes of water, nutrients, organic material, salt and heat transported in the upwelling filament from the Northwest African region into the subtropical gyre and determine its effect on the carbon mass balance of plankton communities. Within this context the cruise undertook different sampling strategies, a long line across the whole archipelago, and then a series of cross sections at different positions through the Cape Juby filament system.

Partial pressure of  $CO_2$  (p $CO_2$ ) along with temperature, salinity and fluorescence were continuously recorded during the cruise. Additionally, samples for pH and total alkalinity (TA) were analysed in the water column of selected stations. pH was measured spectrophotometrically (Clayton and Byrne, 1993) and TA by potentiometric titration (Pérez and Fraga, 1987). Total inorganic carbon (TIC) was determined by the coulometric method described in Johnson *et al* (1993), following the recommendations of the JGOFS protocol (June, 1994). As the sampling density for coulometric TIC was much lower than for TA and pH, TIC was calculated also from pH and TA using the dissociation constants by Lueker *et al.* (2000).

The physical background during the FAX cruise is described in Barton et al. (2002).

As an overview, two upwelling filaments arising from the coast near Cape Juby extended offshore to merge southwest of Fuerteventura and turned southward around a quasi-permanent cyclonic eddy trapped in the through south the inner islands. The filaments were discontinuous as they encountered warm water in the lee of Fuerteventura. At their offshore limit they were partially entrained around the anticyclone shed from the Gran Canaria Island. Another filament persisted in the north of the area throughout the cruise in the Fuerteventura-Lanzarote channel and turned cyclonically southwards.

Along the long line extending from Cape Juby to north of La Palma south of the Canary Islands, one filament arising out of the continental shelf south of C. Juby and several anticyclonic and cyclonic eddies were sampled. Vertical excursions of the main physical variables clearly reveal the eddies, filament and coastal upwelling signal. Surface chlorophyll presented a high concentration in the coastal upwelling area. Offshore, the maximum chlorophyll concentration situated at about 50 m, except for the strong cyclone southeast of Hierro where surface concentrations are higher.

Water column pH, normalized TIC and  $pCO_2$  directly correlate with the density structure, whereas normalized TA presented a more independent distribution.

Upwelling brings to the surface cold, fresh and high  $pCO_2$  waters however, the surface air-sea gradient in this coastal area is negative, towards the ocean, pointing to a biological reduction of  $CO_2$  in the ocean, in agreement with the high chlorophyll concentration in the upwelling coastal area. As well, in the cyclonic eddies or filament crossings  $pCO_2$  is also low compared to the surrounding waters, pointing again to a biological control of  $pCO_2$ .

The surface  $pCO_2$  distribution along the mesoscale samplings crossing the filamenteddy system offshore Cape Juby showed that the region mainly behaved as a  $CO_2$ source. Strong  $pCO_2$  reductions were associated with the upwelling, filaments or cyclonic eddies, where in most cases a high chlorophyll or flourometry signal was encountered.

In order to assess the relative contribution of physico-chemical and biological processes in the surface distribution of  $pCO_2$  we have applied a simple and preliminar methodology as proposed by Sabine and Key (1998) and used by Alvarez *et al.* (1999). This method assumes that the upwelled water near the coast is advected and modified offshore neglecting water mass mixing and air-sea exchange. This water is cumulatively corrected for the temperature change, dilution, organic matter and carbonate production or remineralization. Only stations east of Gran Canaria where surface pH and TA values were available were used in this analysis.

As initial conditions for the upwelled water we took the physical and chemical char-

acteristics of 16°C water. From this initial conditions the following corrections over  $pCO_2$  were applied:

• temperature correction:  $pCO_2$  <sup>T</sup> is calculated as a function of measured temperature, and the initial conditions for salinity (S<sup>0</sup>), alkalinity (TA<sup>0</sup>) and TIC (TIC<sup>0</sup>):

 $pCO_2$   $^T = f(T, S^0, TA^0, TIC^0)$ 

• dilution correction: estimated from changes in salinity, which also affects TA and TIC:

TA  $^{S} = TA^{0} \cdot S/S^{0}$ TIC  $^{S} = TIC^{0} \cdot S/S^{0}$ pCO<sub>2</sub>  $^{TS} = f(T, S, TA^{S}, TIC^{S})$ 

• organic matter correction: biological activity in the area is estimated from changes in nitrate (N). The difference between the measured and reference N is proportional to the biological uptake/regeneration using a given  $R_{C/N}$  ratio. In the case of TA, TA<sup>S</sup> should be corrected for the uptake of one mole of H+ for every mole of N:

$$\begin{split} \mathbf{T}\mathbf{A}^{SN} &= \mathbf{T}\mathbf{A}^S + (\mathbf{N}^0\text{-}\mathbf{N}) \\ \mathbf{T}\mathbf{I}\mathbf{C}^{SN} &= \mathbf{T}\mathbf{I}\mathbf{C}^S - \mathbf{R}_{C/N} \quad \cdot (\mathbf{N}^0\text{-}\mathbf{N}) \\ \mathbf{p}\mathbf{C}\mathbf{O}_2 \quad ^{TSN} &= \mathbf{f}\left(\mathbf{T}, \mathbf{S}, \mathbf{T}\mathbf{A}^{SN}, \mathbf{T}\mathbf{I}\mathbf{C}^{SN}\right) \end{split}$$

- calcium carbonate correction: carbonate dissolution/precipitation affects TA and TIC in a 2:1 ratio. Corrected TIC and  $pCO_2$  for heat and water flux, biological processes and carbonate precipitation/dissolution were calculated as:

 $TIC^{SNCa} = TIC^{SN} - 0.5 \cdot (TA^{SN} - TA)$  $pCO_2 \quad ^{TSNCa} = f(T, S, TA, TIC^{SNCa})$ 

In the former calculations of  $pCO_2$  as a function of TA and TIC the thermodynamic constants from Lueker *et al.* (2000) were used.

If we use a Redfieldian  $R_{C/N}$  equal to 6.6 the pCO<sub>2</sub> residuals' mean value (predictedreal) is 48 ± 8 µatm. However if we use a  $R_{C/N}$  equal to 10.5 the residuals reduce to  $0 \pm 7 \mu$ atm. If we assume that our simple 1D model is correct, this  $R_{C/N}$  high value indicates that organic matter (dissolved or particulated) with a high content in carbon is produced in the upper water column. Particulated organic matter during the FAX cruise presented a  $R_{C/N}$  of  $6.8 \pm 2$ . Therefore, dissolved organic matter enriched in carbon must be accumulated in the euphotic zone. Unfortunately no dissolved organic nitrogen data were analysed to support this conclusion. Despite this, several studies in similar areas support this proposal (Carlson *et al.* 1994, Williams, 1995, Sambrotto *et al.*, 1993).

We are aware of the drawbacks of our simple methodology to discern the processes affecting the  $CO_2$  system in the Canary Islands upwelling region. In the future we will integrate a more elaborated balance for organic and inorganic carbon in the euphotic zone of the area taking into account the different fractions of organic matter and assessing the main factors affecting the budgets.

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