

First estimation of the Oceanic Acidification in the Catalanian Sea

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ABSTRACT The beneficial service of reducing the global warming that the ocean makes by absorbing annually 24-28% of the CO₂ generated by the humankind use of fossil fuel have a side effects in the chemical composition of the ocean, driving to a general decrease of the pH, which has been termed as the 'the other CO₂ problem' or Ocean Acidification (OA). The impact of OA in the biological community is still in debate although there is a consensus that many organisms with CaCO₃ structures will be strongly affected before the end of the century. The OA has not been evaluated in the Catalonia and Balearic Seas because of the scarcity of pH measurements.

In this study, we compare pH measurements done in July of 1983, during the PEP-83 cruise along a section between Barcelona and the Balearic Channel, with observations done in 2009, during the FAMOSO program developed in the northern Catalanian Sea. A rate of pH decrease of 0.00096 ± 0.00045 is determined for this 26-year lapse of time in the intermediate layers (200-500 meter depth) that correspond with the layer of Levantine Intermediate Water (LIW). This rate is about a 55% of the rate expected from the atmospheric CO₂ increase assuming an air-sea equilibrium and about a 60% of the average pH decrease observed in the global sea surface through the main fixed stations (Bates et al. 2014).

METHODS In July of 1983, pH measurements from surface to 500 meter depth were made along the section between Barcelona and the Balearic Islands (red dots in Figure 1). These measurements, made in NBS scale, were referred to 15°C in Pérez et al. (1986) and were converted to pHT₂₅ scale at 25°C using the equilibrium constants of the carbonic system of Mehrbach et al. (1973) used also in Pérez et al. (1986).

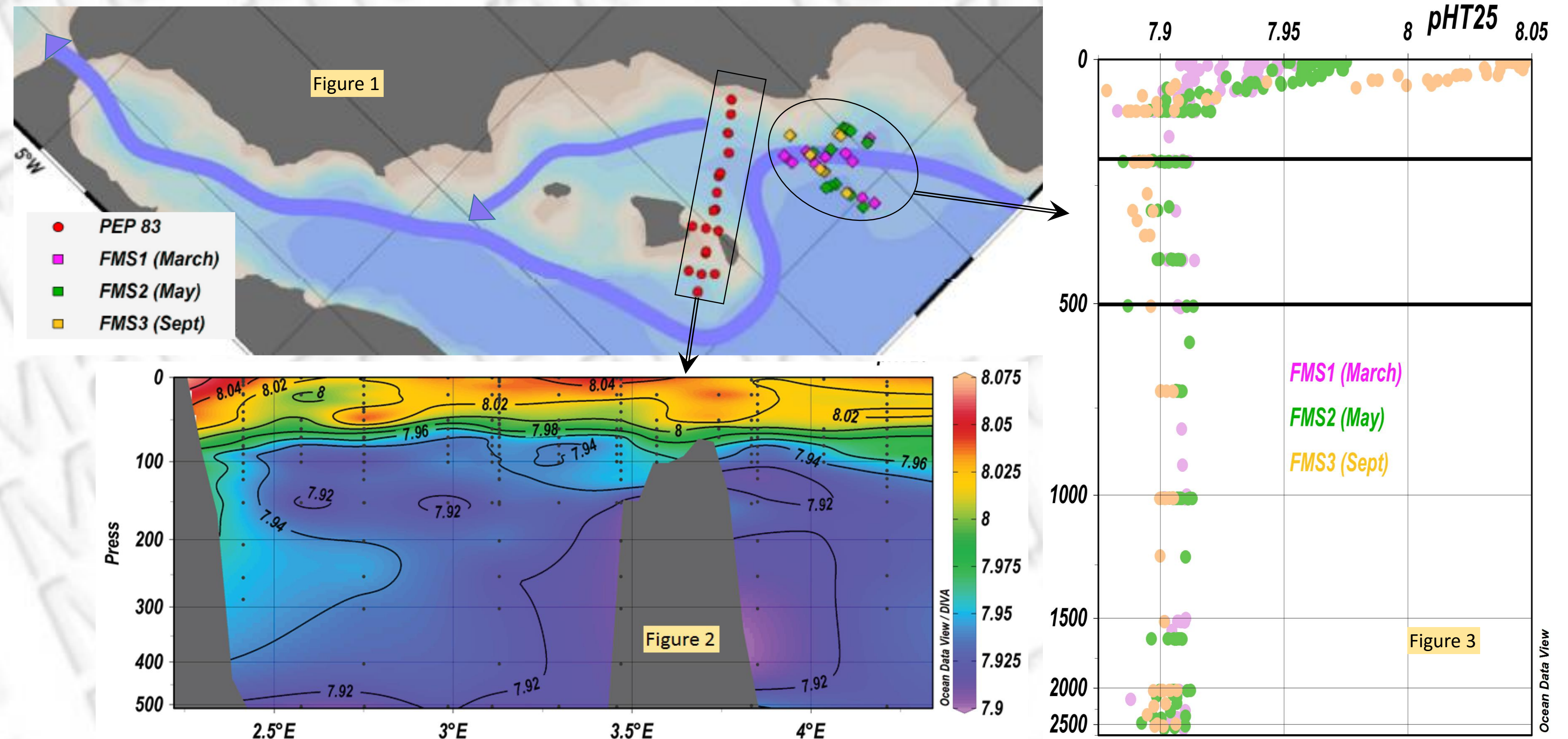
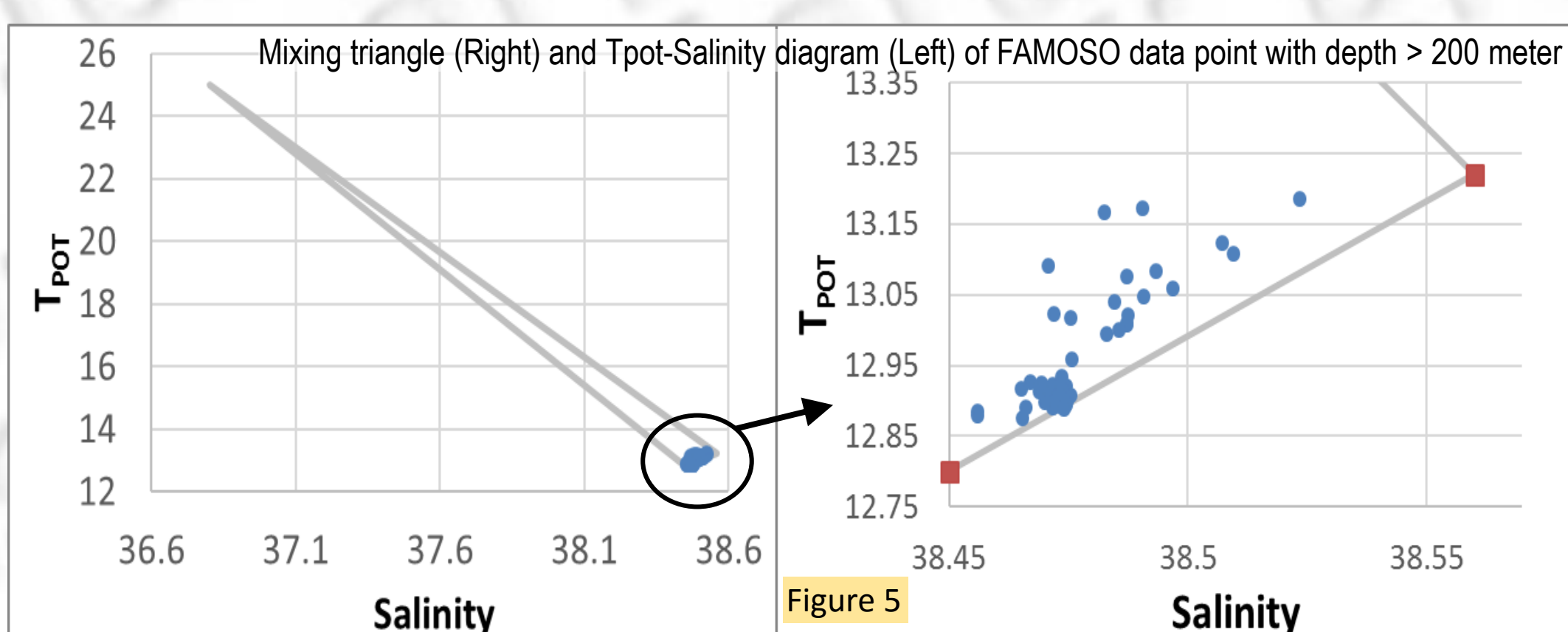
In the three FAMOSO cruises in northern Catalanian Sea (squares fuchsia, green and yellow colors), pH was measured spectrophotometrically in pHT₂₅ scale at 25°C using the Clayton and Byrne (1993) method.

RESULTS (Spatial variation from the Mar Catalan to Gibraltar Strait)

C) Flecha et al (2016) evaluated the pH and the acidification rate in the station GIFT in the Strait of Gibraltar Using the pH observations from autonomous probe (SAMI-pH) and performing an Optimum Multiparametric analysis (OMP) to characterize the pHT₂₅ for Western Mediterranean Deep Water (WMDW) and LIW in 7.9077 ± 0.0004 and 7.8897 ± 0.00037 respectively (Table 2). Considering that the WMDW is formed relatively close to the FAMOSO study area, and that LIW main path is also crossing this area in its cyclonic circulation in the western Mediterranean we perform the same OMP analysis with FAMOSO data to evaluate the downstream changes in pHT₂₅ (Fig. 1). Figure 5 shows the T-S values of WMDW and LIW end-members ($12.8-38.45$ and $13.22-38.56$, respectively), and the T/S values of all samples below 200 meters depth. For the FAMOSO data, the obtained values of pHT₂₅ for WMDW and LIW are 7.9095 ± 0.0012 and 7.9037 ± 0.0030 respectively. These values are slightly higher than those found in GIFT. However we also need to consider the biological activity that produces a decrease of pH and O₂ during the oxidation of the organic matter from FAMOSO to GIFT study areas. Similar OMP using O₂ data revealed a similar decrease of 22 µmol/kg in both water masses which correspond to a reduction of 0.033 pH units using the classical C:O₂=1.45. Adding this biological reduction to GIFT data, the pHT₂₅ of the WMDW and LIW for the time they were in the FAMOSO area is 7.941 and 7.922, respectively. Now the difference in the pHT₂₅ is 0.031 and 0.018, indicating an earlier water mass formation and transit in about two and three decades of the WMDW and LIW, respectively, present in the FAMOSO area.

Table 2. Values of the Oxygen and pHT₂₅ for the water mass type LIW and WMDW

Cruise	Year	Oxygen	pHT ₂₅	
		WMDW	LIW	
FAMOSO	2009	208.9 ± 0.8	186.2 ± 2.0	7.9095 ± 0.0012 7.9037 ± 0.0030
GIFT-SAMI	2012-15	186.7 ± 3.3	164.6 ± 3.1	7.9077 ± 0.0004 7.8897 ± 0.0003
				Here Flecha et al. 2015



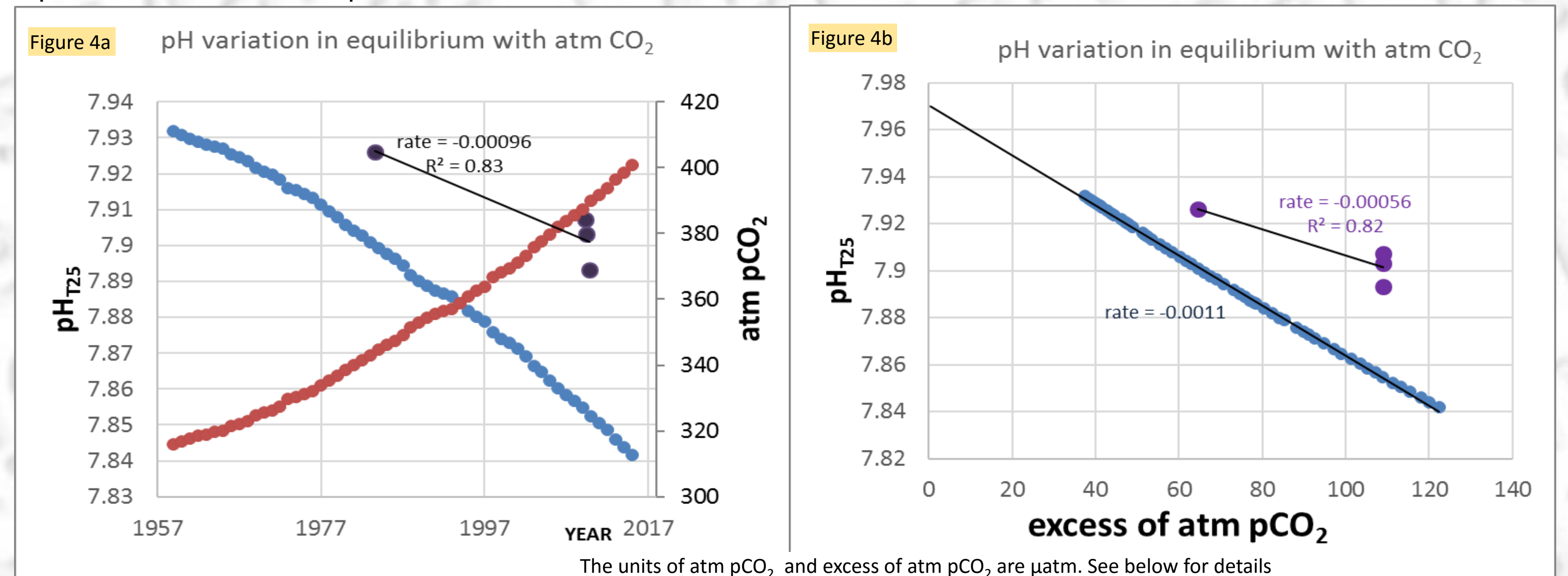
RESULTS (time variation)

A) In July of 1983, surface heating and photosynthetic activity caused high values of pH (> 7.95) within the 80 first meters of the water column (Fig. 2). Below that level, several minima of pH was due to the mineralization of sinking organic matter. The pH observations of 2009 showed the same pattern (Fig. 3): high pH values in the surface layer during September and relatively low pH values in the surface layer in March, when the cooling and vertical mixing were strong. Some profiles also showed a pH minimum around 100 meter depth mainly in September. Deep waters showed very narrow range of variation. To avoid the effects of highly seasonal processes in the long-term OA estimations, we focused in the layer of 200 to 500 meters depth where the variability is very week. In table1 we show the average properties of the 200-500 m depth layer.

Table 1. Average and standard deviation of the main properties for the layer of 200-500 meter depth

Cruise	mm-YY	N	Latitude	Longitude	Depth	Tpot	Salinity	pHT ₂₅
PEP-83	Jul-83	32	40.35 ± 0.67	3.30 ± 0.60	277 ± 70	12.998 ± 0.077	38.373 ± 0.043	7.926 ± 0.015
FMS1	Mar-09	23	41.64 ± 0.26	4.39 ± 0.47	323 ± 112	12.992 ± 0.079	38.481 ± 0.014	7.908 ± 0.003
FMS2	May-09	30	41.70 ± 0.27	4.28 ± 0.41	311 ± 114	13.114 ± 0.085	38.499 ± 0.016	7.904 ± 0.008
FMS3	Sept-09	14	41.61 ± 0.21	4.11 ± 0.33	281 ± 89	13.255 ± 0.078	38.527 ± 0.034	7.893 ± 0.003

B) Figure 4a shows the time evolution of pH in seawater in full equilibrium with atmospheric CO₂ (*atm pCO₂*). pH (blue dots) is computed from pCO₂ and alkalinity using the equations of carbonic system. Values of *atm pCO₂* (red dots in Fig. 4a) are taken from Mauna-Loa Station (Hawaii) (http://ftp.cmdl.noaa.gov/ccg/co2/trends/co2_annmean_mlo.txt). Alkalinity is computed from salinity ($\text{Alk} = 70.81 \cdot \text{Salinity} - 123.9$; Pérez et al. 1986). The averaged mean pHT₂₅ values observed in 1983 and 2009 are also included and the acidification rate, of 0.00096 ± 0.00045 , estimated by linear regression. For the uncertainties, the error of the mean and the accuracy of pH measurements have been taken into account. Fig. 4b shows the pHT₂₅ evolution versus the excess of CO₂ (pCO₂ less preindustrial pCO₂) in the atmosphere. A rate of change of pH per µatm of pCO₂ excess of -0.00056 is obtained which is about 55% of that expected if the water mass was in full equilibrium with the atmosphere.



References

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