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Hourly to Decadal variability of sea surface carbon parameters in the north western Mediteranean Sea

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Sea surface CO_2 fugacity, fCO_2, is recorded hourly in the north western Mediterranean Sea since 2013 by two CARIOCA (Carbon Interface Ocean Atmosphere) sensors installed on the BOUSSOLE (Buoy for the acquisition of long term optical time series, http://www.obs-vlfr.fr/Boussole/html/project/introduction.php) mooring at 3m and 10m depth. fCO_2 exhibits a large seasonal cycle, about 150 microatm peak to peak, very consistent with earlier CARIOCA measurements taken in 1995-1999 at the DYFAMED site (located 6km apart from the BOUSSOLE mooring) (Hood and Merlivat, JMR, 2001; Copin-Montegut et al., Mar. Chem., 2004): this seasonal cycle is driven primarily by intense mixing in Winter, biological uptake during Spring and warming during Summer. Interannual variability of these processes leads to interannual variability of monthly mean fCO_2 that can reach more than 20 microatm. The short term variability (1 hour to 1 week) is large, especially during Summer 2014 (more than 40 microatm) due to a very strong vertical stratification and to the influence of internal waves.

The hourly CARIOCA measurements allow to correctly filter out the high frequency variability while the three year long time series allow to smooth out interannual variability. Hence, for the first time, we get a precise estimate of the change of fCO_2 in surface waters within 20 years. Over the 1995-2015 interval, we estimate an increase of fCO_2 computed at a constant temperature of 13˚C equal to 1.8 microatm per year. Given the alkalinity/salinity relationship in this region, we estimate mean annual rates of change of -0.0023+/-0.0001 pH unit and of +1.47+/-0.03 μmol kg-1 for pH and DIC respectively. These results give a quantitative estimate of the penetration of anthropogenic carbon in the surface waters of the northwestern Mediterranean Sea, about 80% via air-sea exchange and 20% via transport of carbon from the Atlantic across the Strait of Gibraltar as suggested by Palmieri et al (BG, 2015). We estimate that the part of DIC accumulated over the last 18 years represents $\sim$32% of the total change since the beginning of the industrial period.