TESTING SYSTEMS TO MONITOR ATMOSPHERIC CO_2, PH AND PCO_2 IN THE OBSEA SUBMARINE OBSERVATORY

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Abstract— Due to the increase, in last years, of carbon dioxide (CO2) level in the atmosphere we start monitoring with the expandable seafloor observatory OBSEA a variety of parameters related with ocean acidification. Our research team has installed an underwater pH sensor in the OBSEA observatory in order to compare the sea pH data with the CO2 data collected with an atmospheric CO2 sensor.

Keywords— acidification, pH, CO2, pCO2

I. INTRODUCTION

It is now well recognised that levels of carbon dioxide (CO2) in the atmosphere have been increasing since the Industrial Revolution due to burning of fossil fuels, leading to global warming [1]. In fact, the level of CO2 in Earth's atmosphere already passed the critical threshold of 400 parts per million in Mauna Loa, Hawaii on May, 2013 (http://www.esrl.noaa.gov/gmd/ccgg/trends/weekly.html). This is the highest concentration of CO2 that the open atmosphere has sustained in probably around three million years [2] and is a clear signal of the negative impact of humans on the environment and the climate system.

Only part of this anthropogenic CO2 is accumulated in the atmosphere (45%), the rest is taken up by oceans and land in similar parts [3]. Importantly, the oceanic counterpart (during the 2003-2012 decade, 2.9 gigatons of C dissolved in the oceans every year [4]) involves a progressive acidification of seawater, since once dissolved, CO2 intervenes in a series of chemical reactions leading to a lowering in pH [5]. Today, global oceans have already acidified by 0.1 pH units since preindustrial times. Predictions indicate acidification in the order of 0.3 to 0.5 pH units by 2100 and of nearly 0.8 pH units by 2300, a scenario with no obvious precedents over the last tens of millions of years [5]. Such pH reduction could have major effects on marine biota, especially calcifying organisms including coral reef communities, which will be unable to calcify effectively under these new conditions (e.g. [6,7]).

The Mediterranean Sea has certain characteristics that make it especially sensitive to the anthropogenic increase in atmospheric CO2. Owing to the higher salinity of its waters, they have higher alkalinity as well [8], and thus a greater chemical capacity to neutralize acid and take up anthropogenic CO2. On the other hand, the shorter residence time of deep waters [9] implies a rapid penetration of anthropogenic CO2 in this basin.

There is debate, however, on whether the acidification due to the marine absorption of anthropogenic CO2 is taking place more rapidly in the Mediterranean than in the global oceans. In 2011, a first study suggested that the Mediterranean Sea was acidifying faster [10]. However, a more recent study still under review, indicates that even though the penetration of anthropogenic CO2 is occurring faster in the Mediterranean, this does not translate into higher rates of acidification [11].

Compared to open seas, the confluence of multiple processes that takes place in coastal zones makes even harder to predict the future trends of seawater pH and the associated vulnerability in these areas. In coastal zones, acidification can also be caused by other processes including the microbial degradation of organic matter in areas with high nutrient loading, the introduction of acidic river water, and the upwelling of CO2 enriched deep water ([12] and references therein), amongst others.

In this context, and in order to gain insight on the acidification problem in coastal areas of the Mediterranean Sea, we found important to initiate instrumental time-series of pH and other parameters of the CO2 system in seawater at fixed stations of the Catalan Coast. Taking advantage of the unique expandable seafloor observatory OBSEA, located at 4 km off the Vilanova i la Geltru coast (40 km south of Barcelona), at a depth of 20 m in a fishing protected area [13], and as a joint collaboration between the SARTI Research Group (UPC), Institut de Ciències del Mar, CSIC, Monterey Bay Aquarium Research Institute and Institut Català de Ciències del Clima, we are testing systems in OBSEA to start monitoring a variety of parameters related with ocean acidification.

II. TESTBED SYSTEMS

We started by implementing a system to monitor atmospheric CO2 in order to compare it with dissolved CO2 in seawater and to assess potential air-sea fluxes of this greenhouse gas [14]. Ideally, this system should have been installed in the fixed surface buoy that marks the OBSEA position. However, to facilitate maintenance and keep a better control of the system, we installed it in the shore station in Vilanova i la Geltrú, with an air inlet in the roof, and a 15 m Bev-A-Line tube line to the CO2 analyser, a Licor 820 (Fig 1). In combination with data on wind direction, for comparisons with seawater pCO2, we will only use the atmospheric CO2 values during the periods in which the winds come directly from the sea.

Fig 1. Atmospheric CO2 measurement system

In addition, we are also testing a relatively new system to measure pH (Fig 2), which uses ion sensitive field effect transistor (ISFET) technology [15,16]. This system has successfully been used in the past by several research groups (e.g. [17,18]). We are comparing these measurements with those from another autonomous pH sensor, the SAMI-pH from Sunburst Sensors, and with measurements performed in the laboratory using spectrophotometry [19]. So far the system seems to accurately measure pH, being sensitive to abrupt pH lowering events associated to storms and strong seawater mixing.

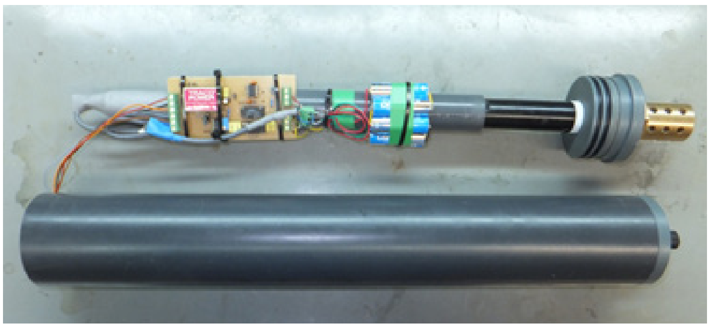

Fig 2. pH sensor based on ISFET technology

Finally, we are also attempting tests with a pCO2 autonomous sensor (Fig 3), a CO2-Pro from Pro-Oceanus [20]. Data from this system, in combination with atmospheric CO2, should allow an assessment of air-sea CO2 fluxes, to evaluate the role of this coastal area as a sink or source of atmospheric CO, a role that probably changes seasonally.

Fig 3. Pro-Oceanus CO2-Pro CO2 sensor

We hope we will be able to have this entire systems operative at the OBSEA cabled observatory in the near future, providing real-time observations of these parameters, perhaps with the possible addition of complementary sensors to allow a more complete determination of all seawater CO2 system parameters. In this sense, the autonomous measurement of seawater alkalinity seems now a real possibility, after the very recent development of the so called SAMI-alk by Sunburst Sensors [21].

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