The Research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 262584, JERICO

# TNA PROJECT REPORT

**1st Call of Proposals**
**12 January – 3 April, 2012**

## *A) General Information*

| | |
|---|---|
| **Proposal reference number**(1) | CALL_1_1 |
| **Project Acronym (ID)** (2) | MEDACID |
| **Title of the project**(3) | Mediterranean Sea ocean acidification time series experiment |
| **Host Research Infrastructure**(4) | POSEIDON BUOYS & POSEIDON CAL |
| **Access to POSEIDON BUOYS**<br>**Starting date - End date**(5) | *If more access period were delivered, please indicate below starting and end date of each period, briefly describing the related activity*<br>3-3-2013 - 6-10-2014 |
| **Access to POSEIDON CAL**<br>**Starting date - End date** | *If more access period were delivered, please indicate below starting and end date of each period, briefly describing the related activity*<br>4-3-2013 - 8-3-2014 Preparation and communication of Sensor<br>18-19 Jan 2014. Sensor is picked up an transported to Gran Canaria<br>14-19 Feb 2014. The sensor is redeployed at the buoy. Discrete surface samples are taken during the research cruise<br>13-15 October 2014. The sensor is picked up and cleaned. |
| **Name of Principal Investigator**(6)<br>**Home Laboratory**<br>**E-mail address**<br>**Telephone** | Melchor González-Dávila<br>Universidad de Las Palmas de Gran Canaria<br>melchor.gonzalez@ulpgc.es<br>+34 928452914 |
| **Additional users** (7) | Magdalena Santana-Casiano, Universidad de Las Palmas de Gran Canaria<br>Magdalena.santana@ulpgc.es<br>+34 928454448 |

## *B) Project objectives (max. 250 words)* (8)

Coastal waters are badly sampled for carbon dioxide and only some CO2 sensors have been recently deployed along USA coastal waters and North of Europe. In this project, the user group is planning to deploy one of its pH sensors having a 0.001 pH unit reproducibility, on one of the buoy of the HCMR POSEIDON networks, placed in an important region as it is the east coastal Mediterranean seawater. Calibration experiments are also planned at the HCMR calibration facility. The project will add great value to:
a) the development of pH measuring system,
b) the monitoring of ocean acidification in the Mediterranean Sea and
c) the JERICO project (both from the point of view of Trans National activities and co-operation and the development of novel and advanced measuring systems).
The main objectives are:
1. Study the daily, monthly, seasonal and inter-annual pH variability in coastal waters.
2. Determination of the main controlling factors affecting the expected acidification.
3. Correlation with physical, chemical and biogeochemical factors controlling the coastal area.

4. Applicability of the pH sensor in coastal areas and for long deployments.
5. Reinforcement of the relations between institutions working in linked activities.

### *C) Main achievements and difficulties encountered (max. 250 words)* [9]

The photometric pH sensor deployed at the Saronikos site developed by the University of las Palmas de Gran Canaria and nowadays commercialized by the company Sensorlab was transported, communication tested and proved in the HCMR, Greece during March 4-8th 2013 by the QUIMA professors in close collaboration with the HCMR group members. On September 10th, after deployment at the Saronikos buoy the sensor started to provide data in real time that were received by the HCMR and weekly sent to QUIMA. The installation, communication, deployment and data transmission processes were perfectly done and excellent results were provided. At beginning of December 2013, no data were provided by the pH sensor and the buoy was recovered, the sensor was picked up by one of the QUIMA members in Athens (18-19 Jan 2014), and transported to Gran Canaria were it was cleaned, an electrovalve was changed (this was the observed problem) and on February 14th the sensor was re-deployed using the Aegean Research Vessel with the participation of the two QUIMA researchers. CT-AT bottles for calibration purposes were sampled at the site. The sensor was recovered on October 6th 2014 and received at Crete by the two QUIMA researchers. After two hours of cleaning and checking the sensor is now ready for a next experience.

By the first time, a photometric sensor was checked to work properly in a long deployment providing accurate data in real time. The sensor provided seasonal, monthly and daily data for surface waters at Saronikos bay.

### *D) Dissemination of the results* [10]

As indicated in C), the results provided by the pH sensor together with the temperature, salinity, meteorological data, and the data for total dissolved inorganic carbon and alkalinity for some discrete samples at the surface waters at Saronikos site are being used to try to publish a scientific work as a collaborative paper among the scientific involved in this TNA. At this moment and due to the fact that the importance of these data is the long time recording and variability, this publication is just starting due to the date of the last recovery.

The results of this TNA were presented during the first year FIXO3 project meeting held in Crete during October 14-16th and Jerico-TNA was referenced.

### *E) Use of the Infrastructure/Installation* [11]

| | In situ | By remote |
|---|---|---|
| **Nr. of Users involved** | 2 | 2 |
| **Access units (days/months/etc)** | CAL: week of 5 days of 8 hours | BUOY: month |
| **In situ stay day / Remote Access duration** | 3 | 18 |

### *F) User project scientific field*

| | |
|---|---|
| **Main field** [12] | Earth Sciences & Environment |
| **Scientific description** [13] | Marine Science/Oceanography |

## *H) Technical and Scientific preliminary Outcomes (max. 2 pages)* [14]

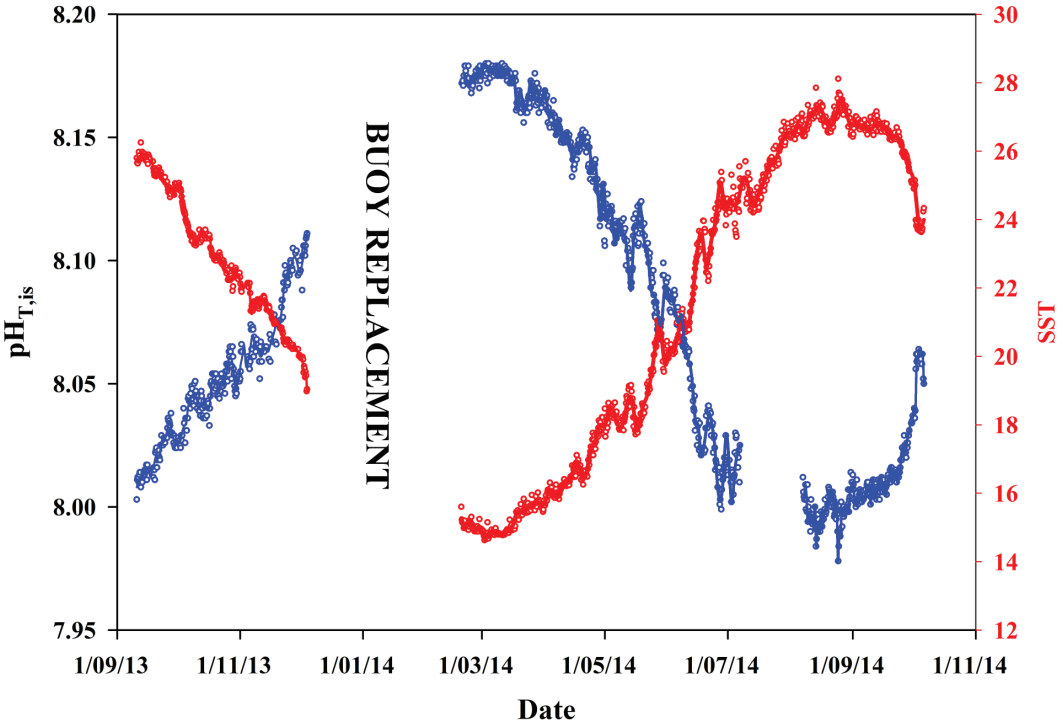
The selected site at the Saronikos Gulf is located at 37.61° N 23.56° E. The Saronikos Gulf is situated in the west-central region of the Aegean Sea, and covers a total surface area of 1,117 $km^2$. The gulf is separated into two basins by a shallow zone (inner Saronikos, depths<100 m); the western basin has depths exceeding 400 m, the eastern basin depths around 100 and 200 m, where the buoy is located. Two small urbanized rivers (Kifissos and Ilissos), discharge in Saronikos but due to obstructive heavy modifications of their flow their discharges become visible only during heavy rainfall.

The surface station of the Saronikos Gulf observing system is a SEAWATCH buoy manufactured by FUGRO OCEANOR. The discus-shaped floating body provides buoyancy and hosts all the electronic modules, the power package and the wave sensor. All the electronic devices are mounted in splash-proof compartment boxes to ensure their safety. Battery powering up the instrumentation is recharged both through solar panels and through wind generator. The observational platform is supported by the scientists and technicians of the Poseidon team (http://poseidon.hcmr.gr) and it is serviced and maintained twice per year using the R/Vs *AEGAEO* and *PHILIA*.

The Saronikos buoy is equipped with sub-surface sensors (4.5 meters below sea level) for currents, temperature and conductivity as well as wave and meteorological sensors (wind speed and direction, air temperature, atmospheric pressure, humidity, wave height and direction). The Oceanlab pH sensor was integrated in the underwater comm port hub of the station and installed at 4 meters below sea surface. The necessary tests and the final configuration were performed before the deployment at the Poseidon technical base in HCMR headquarters at Anavissos.

The gulf is subjected to a strong seasonal cycle of heating/cooling, with air temperatures ranging from 0º to 40ºC. As a result, a seasonal pycnocline is formed from May to November. In winter the water column is homogenized down to 120 m. A circulation study in the area (Kontoyiannis, 2010) has shown that a two layer thermohaline circulation is formed during summer and autumn, while during winter and early spring a barotropic anticyclonic circulation pattern is formed in the upper 90 m.

During our experiment, a full year cycle in sea surface temperature and pH was followed. The temperature from september 2013 to October 2014 ranged from 14.8 at the beginning of march 2014 to over 27ºC from mid august to mid September, where temperatures of 27.5 were also reached by the end of August. As it is expected, temperature and pH at in situ conditions followed a reverse behaviour. Maximum pH values in total scale (it considers the free hydronium ion concentration and that forming the ion paring $HSO_4^-$ species) at in situ condition of temperature, salinity and depth (4 meters) were determined in March 2014, were a value of 8.14 was measured. After that month, the temperature increased and the pH decreased until reach by the end of August values of 7.98. During the period of maximum temperatures, pH values were in the 8.00- 7.98 range. After the last week of September the temperature of the seawater left the 26ºC range and started to decrease, while the pH increased from 8.01 determined by the end of September. It is important to observe that in this Mediterranean Sea area, at the Saronikos Gulf, pH changed seasonally over 0.16 pH units. Compared to other open-ocean regions, Saronikos Site pH variability is higher than observations in the North




Atlantic (8.03-8.14), the Iceland Sea (8.08-8.11), the subtropical North Pacific Ocean (8.06-8.14) and the northeast Atlantic subtropical gyre (8.01-8.05) (Bates et al., 2014). The variability observed here is similar to that observed in the equatorial Pacific with a range of 0.18 units, where seawater pH variability is mainly controlled by upwelling and by a biologically active area. In the Saronikos Gulf, after normalizing the pH values to a constant temperature, in order to remove the thermodynamic effects, a pH of 8.02 ± 0.01 was determined (data not shown) clearly indicating that most of the seasonal pH variability was associated to the seasonal solar heating cycle that produced a change of almost 13ºC in the sea surface seawater temperature. The area of study have been considered to be under an increase in zooplankton abundance and decrease in chlorophyll possibly caused by reduction of anthropogenic nutrient input. However, in this area calcification should also be considered, and due to the alkalinity decrease with calcification, the pH decreases after normalization during late Spring and Summer. If photosynthesis was the main process, dissolved inorganic carbon should decrease and then pH increase, a process not observed in this area during Spring and Summer. These and other aspects related to the explanation of the observed values are now being considered for publication in a scientific paper by the two groups involved in this project.

The continuous pH recording process allowed by the JERICO TNA MEDACID project has allowed us to provide by the first time a high accuracy pH data in an strategic area, show the applicability of photometric pH sensors as important tools for pH monitoring and research and to open a door for better knowledge of the surface ocean under a changing world.