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New pH Sensor for Monitoring Ocean Acidification

QUIMA, SensorLab Develop pH Sensors for Long-Term Operation

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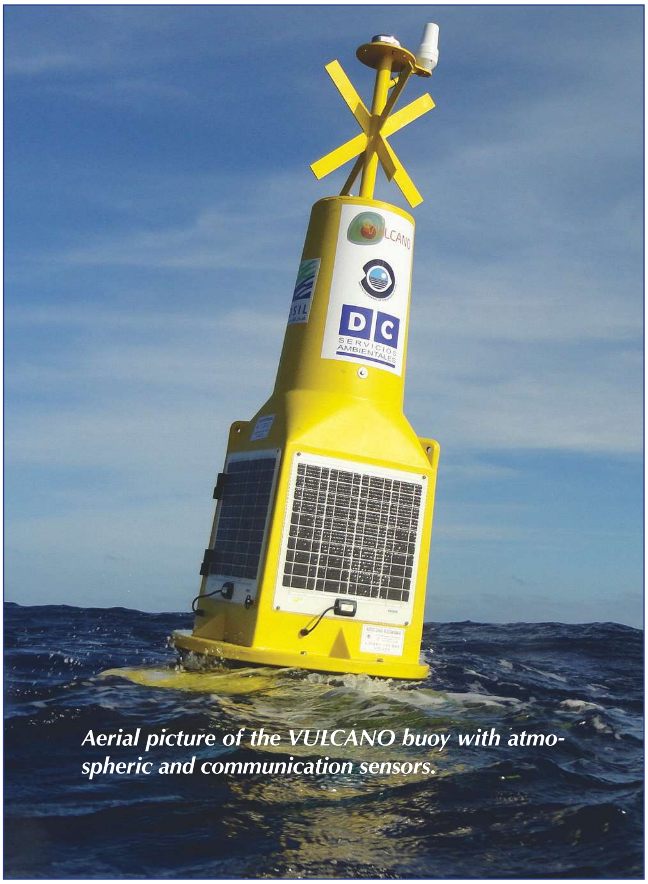
The increase in the production and emission of anthropogenic CO_2 and its absorption by the oceans leads to a reduction in oceanic pH, a process referred to as ocean acidification, which affects many other physicochemical processes. Atmospheric CO_2 is expected to continue its increase, and consequently the chemical changes will likely continue well into the future, affecting the ocean biogeochemical cycling. In order to characterize the ocean's chemical and ecosystem-related changes, examination of CO_2 system parameters over a wide range of temporal and spatial scales is necessary. Shipboard analyses in oceanic time series conducted during irregular ocean expeditions, which lasted between a fortnight and a month, have provided most of our understanding of recent trends in the oceanic CO_2 system. However, our ability to make frequent autonomous measurements over a broad range of spatial scales would greatly augment the current suite of open-ocean and coastal observations.

The carbon dioxide system in natural waters is defined by the measurement of two or more carbonate parameters: pH, carbon dioxide fugacity (fCO_2), total alkalinity (TA) and total dissolved inorganic carbon (DIC). The ocean carbon and ocean acidification research communities have long been craving robust methodologies and in-situ sensor technology for precise carbonate variable measurements. In-situ sensors for pH, pCO_2, DIC and TA of seawater have been developed based in spectrophotometric techniques that in most cases require accurate dye additions and consideration of the effects of aging. The QUIMA group at the University of Las Palmas de Gran Canaria and SensorLab (Las Palmas, Spain) have developed a new family of rugged and extremely stable spectrophotometric pH sensors for both lab-based research and buoy monitoring, specifically designed for unattended operation independently of dye and aging effects in surface waters.

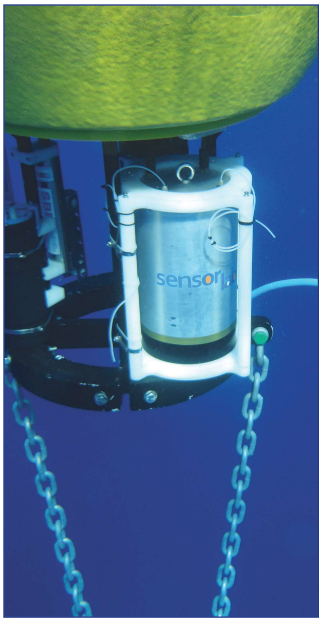
Sensor History

The development of the first lab-based pH sensor prototype was completed by the QUIMA group in 2007. The experience from this first prototype enabled the development of the first submarine pH sensor, completed in 2009.

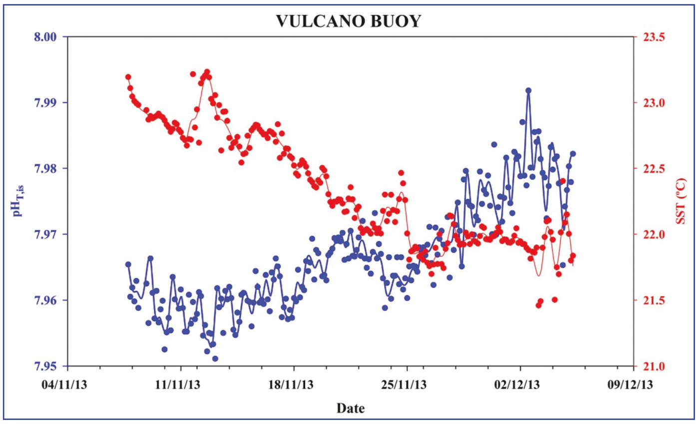


Aerial picture of the VULCANO buoy with atmospheric and communication sensors.

Integrating a spectrophotometric pH system in a standalone, submarine unit was not a straightforward process. Many challenges had to be addressed. Achieving high accuracy in open water proved to be quite challenging, as the pressure changes due to the swell caused small, short-term pH measurement errors. A pressure compensation system was designed and implemented so the undesirable effects of pressure variations fell below the measurement uncertainty. The presence of fouling was a big challenge as well. In addition to the typical obstruction problems, the gas exchange created by the fouling close to the sample intake modified the pH readings. Different anti-fouling coatings and techniques



(Left) Immersed part of the VULCANO buoy with the SensorLab pH sensor. (Bottom) VULCANO buoy record of pH in total scale at in-situ conditions of temperature and salinity (blue dots) and sea surface temperature (SST in °C, red dots) from deployment day November 7 to December 8, 2013. (Right) Saronikos buoy with pH sensor before deployment in September 2013.



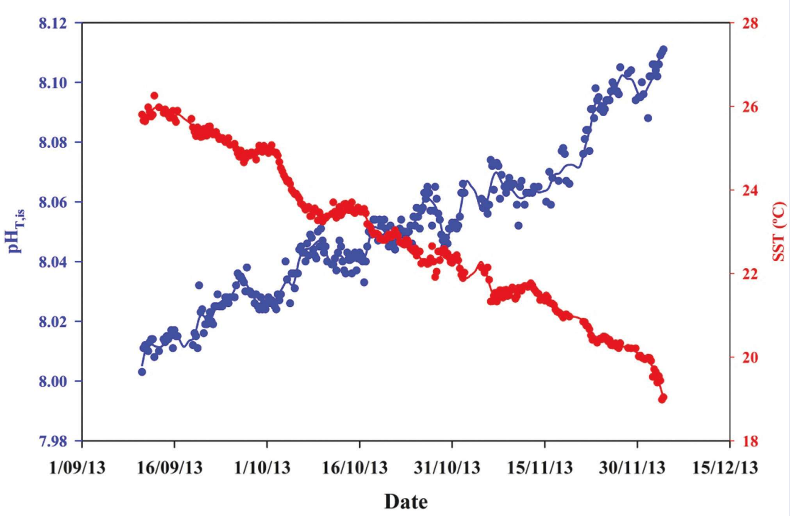
were tested, but most of them interfered with the pH readings. The chosen solution was using ETFE tubing with the sample intake placed at least 1 foot away from the sensor body, which helped to avoid the fouling interference. This proved to be very effective for long-term deployments. All the prototypes developed are still being used today by the QUIMA group and have been used in various scientific publications.

Sensorlab pH Sensors

SensorLab was established in 2011, and QUIMA group prototypes gave birth to the first commercial submarine sensor, the SP100-SM. The experience acquired with this sensor led to the new SP101-SM, packing several improvements over the previous generation of sensors. These improvements included a 40 percent reduction in the sensor power consumption, thanks to a redesigned higher efficiency electronic controller, and a new low-power LED light source. The corrosion resistance has also been improved with the addition of an epoxy coating, plus polyurethane finishing on top of the 6060 hard anodized aluminum housing.

The sensors use spectrophotometric-based methods to measure the pH, removing the dye effect in each determination. The dye used is m-cressol purple.

The design of the pH sensors allows for the same accuracy achievable in the lab, but autonomously deployed in the ocean, enabling long-term measurements without human intervention. As environmental conditions change, the sensor is designed to adjust all the measurement parameters automatically to provide maximum accuracy. An important point to note is that the system also returns the internally calculated error for each measurement. This continuously tracks the system measurement accuracy and can be used as an indicator to plan preventive maintenance cycles. Sensorlab pH sensors are full data logging devices, not only measuring pH but also temperature, using the internal high-accuracy temperature sensor, and salinity, through an optional external thermosalinometer. The units can store up to 19,000 measurements in nonvolatile memory, including the measurement time and date from the included internal real-time clock.



Saronikos buoy record of pH in total scale at in-situ conditions of temperature and salinity (blue dots) and sea surface temperature (SST in ºC, red dots) from deployment day September 10 to December 5, 2013.

El Hierro Submarine Volcano

On October 10, 2011, an underwater eruption gave rise to a novel shallow submarine volcano south of the island of El Hierro, Canary Islands, Spain. In order to monitor the physical-chemical properties of the surface water around the submarine volcano, as part of the VULCANO project (Volcanic erUption at El Hierro IsLand Sensitivity and ReCovery of the mAriNe EcOsystem), the Instituto Español de Oceanaografía deployed, on November 8, 2013, a subsurface buoy capable of measuring in real time the temperature, salinity, oxygen concentration, pH and pCO_2 of the surface water. A SensorLab pH sensor was included in the buoy provided by QUIMA with a sampling interval of three hours. The data were available daily at http://goo.gl/3SI6Nq.

The buoy was provided to the VULCANO project by DC Servicios Ambientales.

Saronikos Sea

As part of the JERICO project (toward a joint European research infrastructure network for coastal observatories), a pan-European approach for a European coastal marine observatory network, which integrates infrastructure and technologies such as moorings, drifters, ferrybox and gliders inside the VII Framework Programme, a transnational action (TNA) was established between the Hellenic Centre for Marine Research and the QUIMA. The TNA planned a deployment of a SensorLab pH sensor in a buoy located south of Greece in the Saronikos Sea. The sensor was deployed on September 10, 2013, and it has been gathering data every six hours at 3 meters depth. The pH in total scale at in-situ conditions of temperature and salinity has increased in

0.1 units of pH due to the decrease in temperature of 7º C. The system is responding to the changing conditions in very oligotrophic waters with salinities as high as 39.

Conclusion

Ocean acidification is a growing concern among the scientific community today. There is still uncertainty surrounding the nature of the effects and consequences of ocean acidification. It could be a threat to the global economy and society, making it a boundless field for research.

The scientific community is demanding and needs access to more ocean pH data, and SensorLab pH sensors are suited for this task. Their performance has been tested and proven through several scientific experiments.

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References

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Dr. J. Magdalena Santana-Casiano studied marine sciences at the University of Las Palmas de Gran Canaria. She graduated in 1988 and received her Ph.D. in 1991. Since July 2010, she has been vice dean of graduate studies. In May 2011, she became a full professor in chemical oceanography. Currently, she is the principal investigator of the ECO-FEMA project and the European CARBOCHANGE project.

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