TNA PROJECT REPORT

1. Project Information

Proposal reference number	JN_CALL_2_5
Project Acronym (ID)	ANB Sensors pHIMS
Title of the project	Testing an Autonomous Self-Calibrating pH Sensor (pHIMS) with On-Board QA/QC, For Ocean and Water Quality Monitoring
Host Research Infrastructure	Ferrybox at m/s Silja Serenade (SILJA SERENADE) Atmospheric and Marine Research Station (Utö) Marine Research Centre Laboratory (SYKE MRC-lab)
Starting date - End date	20/01/2019- 30/06/2019
Name of Principal Investigator **Home Laboratory** **Address** **E-mail address**	Nathan Lawrence ANB Sensors 28 Willow Lane, Great Cambourne, Cambs,CB23 6AA, United Kingdom nlawrence@anbsensors.com
User group members	Nathan Lawrence, Luke Shirley, Brandon McHale ANB Sensors, United Kingdom

2. Project objectives

ANB Sensors are developing the next-generation pH sensor suitable for oceanographic profiling and buoy deployment. The main objective of Jerico-Next TNA project was to test their current sensor version (as of January 2019) at the Finnish Environmental Institute SYKE and at Finnish Meteorological Institute FMI. The lessons learnt in these tests would be put in place for their next generation sensor which has been developed alongside the current TNA project. This version would allow the TRL be raised further ready for commercialisation in late 2019. The key objectives for the Jerico-Next TNA project in collaboration with SYKE and FMI were to:

• Provide feedback on the sensors ease of use, ease of deployment and data retrieval features.

• Debug the sensors highlighting any key issues associated with the sensor performance and use.

• Validate the sensors response against independent measurements in real time deployment.

• Deploy the sensor in a variety of conditions.

• Raise the TRL to 8/9 through Beta testing.

• Allow ANB Sensors to understand the issues associated with oceanography and sensor deployment for other analytes – providing scope for future collaborations.

3. Main achievements and difficulties encountered

The projects main achievement was the successful testing and de-bugging of the sensor in a live system. From both the evaluation of the data retrieved from our sensor, along with a better understanding of today’s current sensor offerings, this work has been invaluable in allowing ANB

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Sensors to further raise its TRL enroute to producing a commercial product in late 2019.

These were the first tests of the system in live media with varying salinity (5ppt to 17.3ppt). By interrogating samples from stations along the ferry Finnmaid voyages it was shown the sensor response suffered no detrimental effects.

The sensor was deployed under a variety conditions, laboratory, on-board a ferry and remotely at an island station. Each location demonstrated the sensors ease of use, with its plug and play technology and ability to retrieve data through removal of the on-board memory card, with a wireless communication capability planned for future versions.

External validation of the sensors response was sought through connecting the system in a flowline with two commercial sensors, a AFT Sunburst pH sensor and a Contros pCO_2. However, on doing this a noise caused by the pumps in the Contros system was seen, so the pCO_2 was removed and the tests continued. Despite this, the system still suffered higher than expected signal-to-noise issues, so new electrodes were produced to maximize the signal. In addition a new electronic design has since been manufactured to enhance the signal, and these electronics are already being deployed in the next generation sensor.

4. Dissemination of the results

Utilizing the data and results gathered throughout this Jerico-Next TNA project, in conjunction with our *in-situ* lab-based research, an academic peer-reviewed article detailing the current electrode composition and measurement technique will be published. In addition, the data will be communicated through conference/meeting presentations in order to demonstrate the validity of our system, and for public, through social media like Twitter. Finally, the results and data will be gathered to procure intellectual property on resulting technologies directly resulting from this research project.

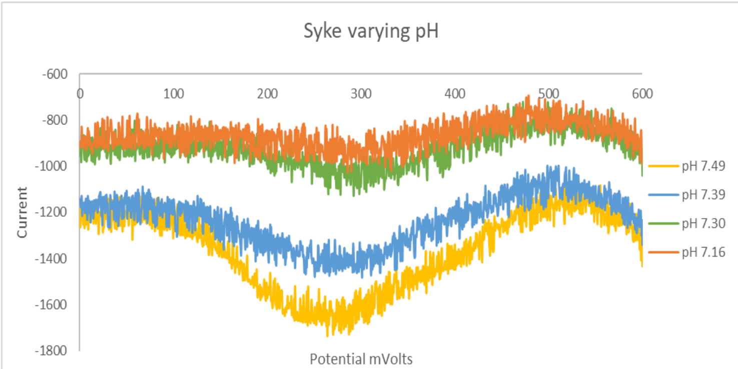
5. Technical and Scientific preliminary Outcomes

The experimentation for this project was conducted over three platforms, Syke MRC-lab, Silja Serenade ferry and the fixed platform at FMI Utö Atmospheric and Marine Research Station.

During the initial phase of testing at the MRC lab in Syke, we first obtained a baseline set of results using a commercial potentiostat. This gave us an indication of the expected results for the complete sensing system when placed in stagnant brackish Baltic Sea water. By utilizing the varying stations from the Finnmaid voyages, we were able to see the effects of a large gradient of salinity (5-17.3). These cover the ranges observed on the Island and ferry test locations. Prior tests at ANB Sensors facilities had shown the sensor operates effectively in ocean salinities (35 ppt). The apprehension going into the testing was that the lower end salinity may affect the conductivity of the system creating problems for the measurement in these areas. However, the conclusion of this demonstrated that our system was able to handle the lower values of salinity.

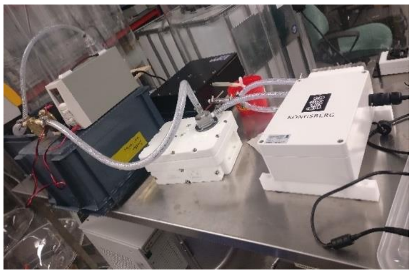
Following these open water tests we integrated our sensor into a flow loop system, shown in the figure. Overnight testing demonstrated the systems ability to handle the relevant pressure (1 bar) and flow rate (5 liters per minute). The integration of the sensor into the flow set-up was tested for approximately 25 days in the lab with both teams present to pass on knowledge of the operation of the instrument.

With confidence in the sensor performance in the flow loop, the next step was to simulate the acidification of the ocean waters in the lab. To this end, two processes were trialed; the first was the addition of CO_2 gas to the water samples collected. However, this route posed difficulty in achieving constant and appropriate steps in pH for a calibration to be achieved. Considering this, the pH change was achieved by addition of carbonated water. This technique was much more controlled and gave the potential/current plots shown in the figure for different pH waters, validated by the AFT-pH system.

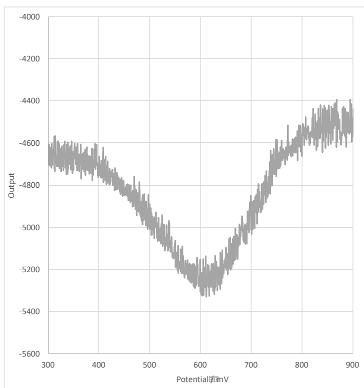


During these trials both the pH and reference signals began to drift over time, and since the drift was consistent for both electrodes, it was suspected that the Ag reference electrode had been damaged or worn away. After analyzing the photos sent by the Syke team, it was apparent that the coating had been worn away and a leak path had been found on the original design. A redesign was rapidly produced and shipped to the lab where it was exchanged for the old design to solve this issue.

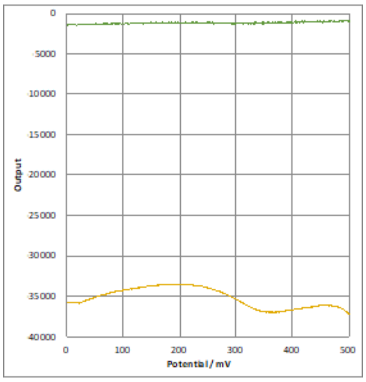
Following the redesign, a more robust test of the lab flow system was trialed with a flow loop containing the ANB Sensors pH sensor, the AFT Sunburst pH sensor and the Contros pCO_2, shown in the figure. However, on doing this a repeating noise within the data was seen which, on further investigation, was seen to be caused by the membrane in the Contros system, so for the remaining tests the Contros pCO_2 was removed from the flow loop. The data was found to respond to changes in the pH of the solution and although not all the experimental plan was completed (temperature studies), the data retrieved from these tests has been invaluable in understanding how the sensor performs under these conditions.



For the remainder of the project, one system was loaded on to the Silja Serenade, the set-up of which is shown in the figure. The second system was placed on the Utö platform. In each case the sensor was placed in a flowline where sea water was drawn in directly from the environment and passed over the sensor interface. The data obtained from the Silja Serenade was found to suffer from noise issues, through the external equipment within the flowline. Despite this, the electrodes were tested on their return to the ANB Sensors laboratory and showed a response in a commercial seawater system. The lesson learnt from this is to increase the shielding and grounding on the electronics



board of the sensor. This recommendation has already been incorporated into the next version of the sensor which is due to go to further trials in June 2019. The results from the Utö station were more encouraging, with the system showing discernable peaks particularly for the system deployed to monitor the drift in the reference system – the common cause of drift in electrochemical based pH sensors.



This is shown in the figure, where the potential of the reference system is given by the peak minimum value in the data. Through the information gathered within this project, a new revision of the ANB Sensors pH sensor has been developed. The feedback on the ease of use, deployment, and ease of data retrieval has all been positive. All debugging issues have been resolved. The final figure highlights the improvements made in the new system, which compares data taken from the SYKE sensor (green) and our pre-commercial sensor (yellow). Through understanding the responses obtained in the real world media, we have enhanced signal, improved the stability of the electrodes and longevity of the sensors, whilst lowering the noise on the system. With the deployment of the sensor in the Utö station and Silja Serenade we have been able to collect real-world data that has allowed for the next revision to increase the TRL and allow for commercialization in late 2019.

SUBMITTED, 10 JUNE 2019; FINAL REVISION, 6 AUGUST 2019