TNA PROJECT REPORT

1. Project Information

Proposal reference number	JN-CALL 1_9
Project Acronym (ID)	CarbonAS
Title of the project	Seasonal variability in carbonate chemistry in the southern Aegean Sea
Host Research Infrastructure	Poseidon Ferrybox (PFB)
Starting date - End date	28 March 2018 – 5 April 2019
Name of Principal Investigator **Home Laboratory** **Address** **E-mail address**	Andrew King Norwegian Institute for water research (NIVA) Gaustadalléen 21, NO-0349 Oslo, Norway andrew.king@niva.no
User group members	Andrew King, Sabine Marty, Caroline Mengeot Norwegian Institute for water research (NIVA)

2. Project objectives

The anthropogenically-driven rise in atmospheric CO2 has potentially significant consequences on marine ecosystems. We planned to deploy a state-of-the-art spectrophotometric pH sensor (AFtES – Automated Flow through Embedded Spectrophotometry) on the host institution's FerryBox sensor system to measure pH and to better elucidate seasonal variability in carbonate chemistry of the southern Aegean Sea – a region of large variability especially with regards to dust deposition and salinity gradients. Through this project, we added high precision pH observations to the suite of measurements that are already part of the Poseidon FerryBox infrastructure, therefore better characterizing the carbonate system. The project was a valuable opportunity to contribute significantly to both instrumental development for surface monitoring and determination of CO2 fluxes in an important region of Mediterranean Sea with unique biogeochemical and water mass characteristics.

3. Main achievements and difficulties encountered

A spectrophotometric pH sensor was deployed on the H/S/F Festos Palace FerryBox that transits between Heraklion, Crete and Piraeus, Greece. The installation was carried out by Sabine Marty and Caroline Mengeot (Fig. 1). The sensor successfully collected pH data on ~100 trips between March and June 2018. The data preliminarily shows that while pH is relatively spatially homogenous between Crete and Greece, the nearshore regions on both the northern and southern end of the transect were slightly lower in pH (~0.02). From March to June, pH exhibited seasonal variability of ~0.2 pH units in the study region from ~8.05-8.15 in March to ~7.95-8.00 in June. pH observations during the remainder of the access period were limited due to a sensor malfunction (leaking due to a cracked faceplate) and FerryBox system electrical/PC issues. The shipment of the sensor from Norway to Greece encountered some unexpected delays due to customs and temporary export.

The activity described in this report has received funding
from European Commission's H2020 Framework Programme
under JERICO-NEXT project, grant agreement No. 654410.

Fig. 1. Sabine Marty (NIVA) installing the pH sensor on H/S/F Festos Palace FerryBox on 27 March 2018.

4. Dissemination of the results

The pH observations supported by the TNA activity will be published in a peer-reviewed journal together with quality controlled FerryBox data from HCMR.

5. Technical and Scientific preliminary Outcomes

Despite the shorter than expected observation period, several interesting preliminary findings have emerged through the CarbonAS TNA activity. Surface water pH observations from March to June 2018 in the middle of the transect (~ 36-37 deg N; **Figs. 2 and 3**) were relatively homogenous. In the coastal regions closer to shore near Heraklion and Piraeus, pH tended to be a ~0.02-0.04 of a pH unit lower. This could be due to ventilation of deeper waters where remineralization has reduced pH – but this needs to examined more carefully and confirmed. From March into June, pH was observed to decline from maximum values of ~8.15 in March and minimum values of ~7.95 in June. This represented a decrease of ~0.2 pH over three months – this magnitude of decline was also observed by buoy-based pH measurements in the Saronikos region of the Aegean Sea which spatially corresponds to the northern section of the H/S/F Festos Palace FerryBox transect (buoy location ~37.6 deg N and 23.6 deg E; observed seasonal variability in pH (total) in 2014 was 8.18 to 7.98; Gonzalez-Davila et al., 2016). Surface temperature during the observation period increased from ~16.5-18.5 deg C to 24-26 deg C (**Fig. 4**), and the decline in pH was coupled with this warming (**Fig. 5**). Based on calculations using CO2SYS (Pierrot et al., 2006) and an average AT of 2630 µmol kg-1 (Gonzalez-Davila et al., 2016), the ~6.5 deg C thermodynamic warming effect on pH between March and June was not able to account for the observed ~0.2 pH decline. This therefore suggests that this region is a sink for CO2 during this time of year. Further analysis will be performed based on a reference samples for total dissolved inorganic carbon and total alkalinity analysis collected in June 2018 (pending at HCMR Athens lab), as well as delayed mode quality controlled data from the Poseidon fixed station (buoy) sensors.

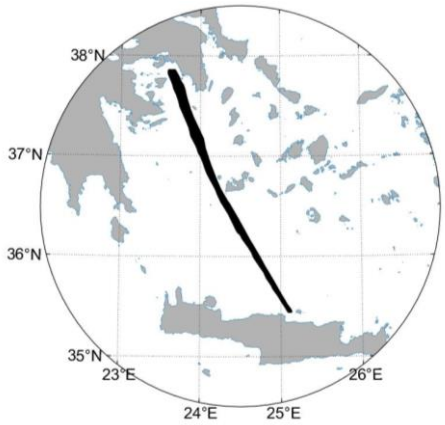

Fig. 2. Ship track of H/S/F Festos Palace between March and June 2018. There were ~100 trips between Heraklion and Piraeus during this time.

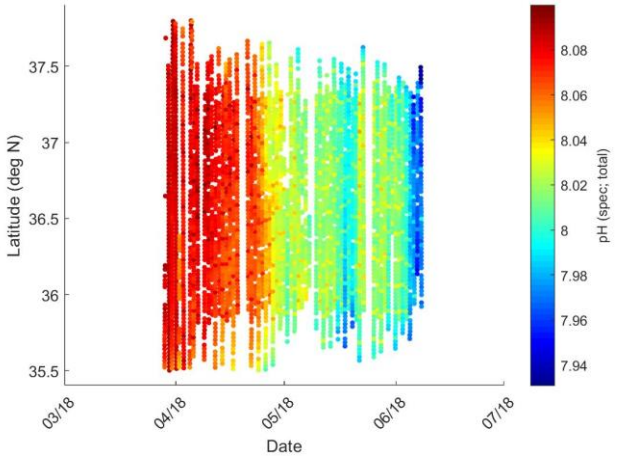

Fig. 3. Spectrophotometric pH measurements (total scale) between March and June 2018 plotted against latitude (deg N) of the transects shown in Fig. 2.

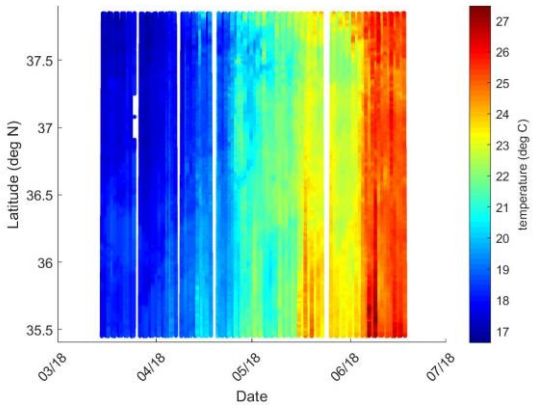

Fig. 4. Sea surface temperature measured by the FerryBox system between March and June 2018 plotted against latitude (deg N) of the transects shown in Fig. 2.

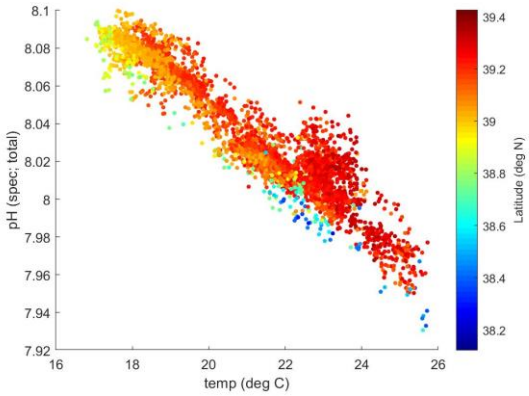

Fig. 5. pH (total scale) plotted against sea surface temperature. Color of symbols indicate salinity at that datapoint. A strong dependence on temperature is observed.

References:

González-Dávila, M., Santana-Casiano, J. M., Petihakis, G., Ntoumas, M., Suárez de Tangil, M., and Krasakopoulou, E. (2016) Seasonal pH variability in the Saronikos Gulf: A year-study using a new photometric pH sensor, J. Mar. Syst., 162, 37–46, https://doi.org/10.1016/j.jmarsys.2016.03.007.

Pierrot D, Lewis E, Wallace DWR (2006) MS Excel program developed for CO2 system calculations. ORNL/CDIAC-105a. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, TN, doi: 10.3334/CDIAC/otg. CO2SYS_ XLS_CDIAC105a.

SUBMITTED, 21 MAY 2019; FINAL REVISION, 4 JUNE 2019.