1. Project Information

Proposal reference number[1]	22/1002926
Experiment Acronym (ID)[2]	CABS
Title of the project[3]	Capacity Building for Autonomous Biogeochemical Sensing in the Southwest Black Sea
Host Research Infrastructure[4]	Helmholtz-Zentrum hereon GmbH
Starting date - End date[5]	1.11.2023 - 11.11.2023
Name of Principal Investigator[6] **Home Laboratory** **Address** **E-mail address** **Telephone**	 Dimitar Berov Institute of Biodiversity and Ecosystem Research 2 Juri Gagarin Street, Sofia, Bulgaria Dimitar.berov@gmail.com ++359885112171

2. Project objectives[7] (250 words max.)

Our project aims at the eventual integration of automated FerryBox type monitoring of water quality in the work of the partner laboratory (LME-IBER-BAS), as a continuation of the ongoing water quality monitoring campaigns of the research institute.One goal of this project is to apply current autonomous methods of EOV observations to a Jerico-S3 FerryBox station, with the intention of using such methods at oceanographic facilities at the Black Sea coast. In particular, we are interested in applying for the use of automated nutrient sensors and automated carbonate system sensors, as well as FerryBoxes. The primary goal is to study the effect of eutrophication on sea grass beds and biodiversity along the southern Black Sea Coast. In particular, we are interested in applying for the use of automated nutrient sensors and automated carbonate system sensors, as well as FerryBoxes. Automated measurements of inorganic nutrients can significantly enhance our understanding of the state of eutrophication beyond the monthly surveys currently in place. Another goal is to enhance our understanding of the effect of seagrass beds, mussel beds and macroalgal ‘forests’ on the carbonate system along the southern Black Sea coast. We intend to use this collaboration with Hereon, to further enhance our observational capabilities in these EOVs, but also to further our collaboration with our German partners. Hereon’s long-term experience in coastal ecosystems monitoring, and the use of automated systems will help us achieve these goals.

[1] Reference number assigned to the proposal by the TA-Office.
[2] User-project identifier used in the proposal.
[3] Title of the approved proposal. The length cannot exceed 255 characters
[4] Name of the installation/infrastructure accessed with this project. If more than one installations/infrastructures are used by the same project, please list them in the box.
[5] Specify starting and end date of the project (including eventual preparatory phase before the access).
[6] Fill in with the full contact of the Principal Investigator (user group leader).
[7] Write the short-term, medium and long-term objectives of the project. Use no more than 250 words.

3. Main achievements and difficulties encountered (250 words max.)[8]

Main achievements:

1. Our team received a thorough demonstration and initial training on procedures of use of automated ferry box –type systems, including maintenance of the system, calibration procedures- discrete samples collection and subsequent lab analysis, data management systems and data processing procedures
2. We've evaluated the pros and cons of the use of the different automated systems at Heren, as well as got familia with the technical, and financial challenges of adopting an autonomous monitoring system with optote sensors for physical and biological parameters (temperature, pH, pCO_2, turbidity, salinity, chl-a), as well as automated nutrient analyzer use.
3. We've discussed in details and made concrete plans for actual sites of deployment of such instruments at suitable locations in the area currently monitored in IBER-BAS water monitoring program (Sozopol, Burgas Bay).

Main identified difficulties:

1. The adoption of such system requires the employment of a highly trained technical personnel that can maintain and calibrate the system
2. We've identified possible difficulties in installing the system at a suitable location that is in close proximity to the water bodies that we are monitoring, that has access to electricity, and that is secure enough for the equipment to be left unattended for long periods of time.

[8] Describe briefly the main achievements obtained and possible impacts, as well as possible difficulties encountered during the execution of the project. Use no more than 250 words.

4. Dissemination of the results[9]

5. Technical and Scientific preliminary Outcomes (2 pages max.)[10]

1. Goal of work

The primary goal of the work was to receive demonstration of the use of autonomous measurement systems for investigating essential ocean variables, and determine how these can be applied for oceanographic measurements in the Black Sea. In particular, the CABS project focused on the use of a FerryBox system, as well as the autonomous measurements of pCO_2 using membrane-based sensors, and automated nutrient analyzers. In addition, information was provided on the applications of using the high-frequency dataset these systems generate, with presentations of recent work by PhD student Louise Rewrie (time series analysis, and the carbonate system of the Elbe estuary), Postdoc David Kaiser (Influence of heat waves on the biogeochemistry of the German Bight adjacent to Cuxhaven station), and an introduction by Yoana Voynova of the Cuxhaven station, relevant biogeochemical characteristics and recent results, including summary recent projects, like JERICO-S3.

In addition, the laboratory in Sozopol, western Black Sea coast, Burgas Bay, was presented by Dimitar Berov, Nikola Bobchev and Stefania Klayn. They introduced the site, and related projects, and specifically ones connected to coastal benthic ecosystems studies, and pollution impacts. Emphasis was placed on the regular (weekly) monitoring in place, which could then benefit from applications of more automated observation systems, to collect data in between the existing monthly sampling.

2. Cuxhaven site

The Cuxhaven FerryBox Station was established in 2010, at the mouth of the Elbe Estuary. It hosts a large FerryBox system, designed by 4H-Jena Engineering (Jena, Germany), which measures a number of parameters (Table 1). Most parameters were already available in the summer of 2010, or by the start of 2011. Water is pumped into the station using a ground-water scale pump, with a flow of at least 80 L/min. The pump is located at a depth of about 5 m. The station is located on a pier close to the main channel of the Elbe discharging into the German Bight (Figure1). This location has restricted access, and is therefore secure.

The HydroC-FT CO_2 sensor (4H Jena Engineering) was installed in 2022 at the Cuxhaven station in order to address the aim of the CABS proposal. This new installation is now planned to contribute measurements to ICOS-D, after Cuxhaven became a pilot estuarine ICOS station in 2023.

[9] Describe any plan you have to disseminate and publish the results resulting from work carried out under the Transnational Access activity in JERICO -S3: scientific articles, books - or part of them -, patents, as well as reports and communication to scientific conferences, meetings and workshops. Highlight peer-reviewed publications. **Note that any publications resulting from work carried out under the JERICO -S3 TA activity must acknowledge the support of the European Commission – H2020 Framework Programme, JERICO -S3 under grant agreement No. 871153.**

[10] Describe in detail results and main findings of your experiment at the present stage.

A nutrient wet chemistry autoanalyzer provided by Systea was re-installed at Cuxhaven prior to the visit during CABS (spring 2023), after a break of about 1-1.5 years in measurements. Automated measurements (about every hour) for nitrate, nitrite and phosphate from a Systea Micromac analyzer were available during the CABS visit, and additional nutrient samples were collected for comparison. Unfortunately, during the CABS visit, the SEAL-500 nutrient autoanalyzer at Hereon was not working, and the samples had to be analyzed at a later stage.

Figure 1. Location of Cuxhaven Station (source: Google and HCDC, Hereon).

During the visit at Cuxhaven, Hendrik Rust and PhD student Louise Rewrie demonstrated the maintenance and sample collection procedure adopted by Hereon for operating a time-series station like Cuxhaven. As a result, this training allowed to experience the automated measurements onsite, including for pCO2, nutrients, dissolved oxygen, and turbidity. Additional samples were collected on site, and the importance of discrete samples for quality control of these parameters were discussed. In addition, samples for dissolved inorganic carbon (DIC) were collected, as part of the routine sampling of the carbonate system at Cuxhaven, with the goal to demonstrate the method of DIC measurement in the lab by the end of the visit.

Table 1. Measured parameters available at Cuxhaven Stationary FerryBox

Measured Parameter(s)	Instrument	Depth / Elevation (m)	Reported Sampling Frequency	Real-time	Start Date
NO2, NOx, NH4, o-PO4, SiO2	Systea Nutrient Analyser (wet chemistry)	-5	10 min	yes	2011
Turbidity (FTU)	Turbidity Sensor	-5	10 min	yes	2011
pH	pH glass electrode	-5	10 min	yes	Summer 2010
Dissolved oxygen	Aanderaa Optode	-5	10 min	yes	2011
Chlorophyll-a fluorescence	TriOS Fluorometer, Turner Flurometer	-5	10 min	yes	Summer 2010
Temperature, salinity	FSI sensor	-5	10 min	yes	Summer 2010
Temperature, salinity	SBE45 sensor	-5	10 min	yes	2020
Intake Temperature	pte100	-5	10 min	yes	2011
CDOM	TriOS CDOM Fluorometer, Turner Cyclops	-5	10 min	yes	2011
Pressure at intake	Pressure sensor	-5	10 min	yes	2011
Housekeeping Parameters	Flow main (FB), Flow in, Flow out	-5	10 min	yes	2011
Global radiation	PAR sensor	10	10 min	yes	2011
Discrete samples (nutrients, salinity, DIC/TA, turbidity)	ISCO Sampler	-5	1-2 months	no	2012
pCO2 (uatm)	4H Jena Engineering HydroC-FT CO2	-5	10 min	yes	August, 2022

3. Results - time series

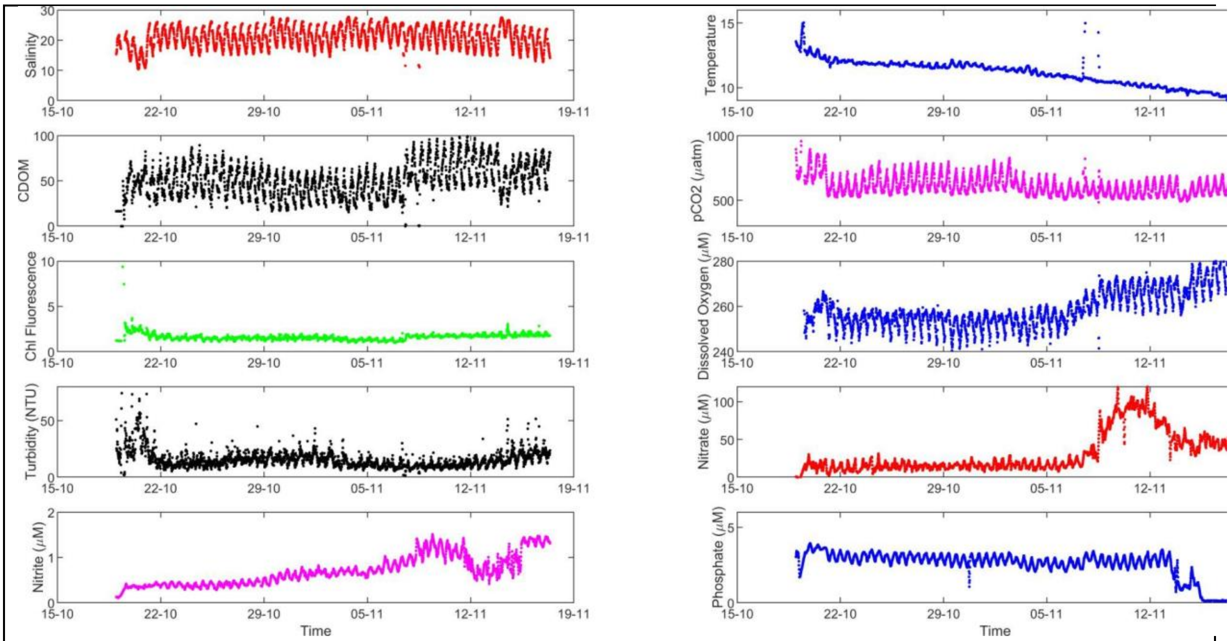

Figure 2. Measured parameters before, during and after the CABS on site participation and sample collection (15.10-19.11, 2023). Parameters shown include salinity, water temperature, CDOM fluorescence, pCO2 (µatm), chlorophyll a fluorescence, dissolved oxygen (µM), turbidity (NTU), and nutrients measured via Systea nutrient analyser (nitrate, nitrite and phosphate in uM).

The measured parameters at Cuxhaven station shown in Fig. 2 were downloaded within the CABS project participants, as a result of the collaboration. In order to get a better idea of the local variability, data for about 1 month of deployment at Cuxhaven was selected. Compared to the western Black Sea, Cuxhaven station results show large tidal variability dominating the signal of all parameters in Fig. 2. In addition, we can observe temperature decrease, and concomitant increase in dissolved oxygen concentration, likely driven by the temperature change. During the Cuxhaven visit (6-7 November, 2023), the optical sensors were also cleaned, which raised slightly the chlorophyll a fluorescence and CDOM fluorescence signals as a result. The trends in the rest of the parameters in Fig. 2 did not change during and after the Cuxhaven visit and service. Nitrogen (nitrate and nitrate in uM) increased after the visit, but this signal should be further investigated when comparing these measurements to the discrete samples. Respectively, phosphate did not increase, but instead, the phosphate signal seems to have been affected at the end of the period after 13. November. This is most likely due to a technical problem with the phosphate measurements, since the tidal variation also disappears. Based on these measurements however, it seems that this site in late fall has relatively high nutrients, but lower seasonal chlorophyll content. Most likely, this could be associated with the high turbidity, and low daylight available during this time.

In comparison, our site at the western Black Sea - a nontidal sea , and an area with no direct influence from river waters inflows, is significantly less turbid, so light limitation from turbidity in the water column is not limiting the phytoplankton development. Rather, the seasonal variations in phytoplankton is driven by changes in inputs of nitrates and phosphates, with well pronounced early spring and summer peaks, and low concentrations in autumn and winter. Nitrate and phosphate concentrations at Sozopol are an order of magnitude lower than those at the Cuxhaven site. Nitrates vary in the range between 0.1 and 4.5 uM.l-1 , while phosphates are usually between 0.1 and 1.0 uM.l-1.

The comparison of the discrete samples processed in the lab and the FerryBox data in Fig. 2 will take place at a later stage, due to the short CABS visit, which did not allow for all samples to be processed during this project.

4. Calibration procedures

Discrete samples for dissolved oxygen, DIC, nutrients, temperature and salinity were collected at Cuxhaven station during the CABS project, using the available ISCO sampler. The samples were brought back to the laboratory, and the lab-based measurements were demonstrated on site. Due to the limited time available, and the unavailability of the SEAL nutrient autoanalyzer, only samples for DIC (6), dissolved oxygen (3) and salinity and turbidity were analyzed. Nevertheless, the methods for these discrete sampling used for quality control were explained, and the training was useful to help understand the effort required for the external quality control of the autonomous methods discussed in the CABS project. As a comparison, the weekly sampling in Sozopol and surrounding area for nutrients uses manual wet chemistry methods, which limits the amount of samples that can be analyzed in the laboratory.

At the end of the visit at Cuxhaven, Hereon Postdoctoral Researcher Vlad Macovei presented data management approaches for quality controlling the autonomous high-frequency data obtained from the FerryBox, and from the pCO_2 membrane-based systems. This was of great interest due to the approach used and considerations for proper quality control of such systems, as well as the needed information regarding the effort required for quality controlling similar large datasets. This knowledge is important when considering the personnel effort needed to generate quality controlled datasets when applying for autonomous systems such as the FerryBox.

5. Discussion of feasibility of application of Ferrybox in Sozopol monitoring

a. Land-based monitoring

Based on the practical experiences and discussions during our visit to Hereon, we identified a number of practical criteria and issues for the selection of possible sites for a coastal ‘FerryBox’-type of monitoring station. The coastal site needs to have direct access to the marine waters of interest, possibly away from local point sources of influence (e.g. sewage or rain water discharge points, port activities). The site where the instrumentation will be mounted needs to be easily accessible, preferably with road access. It also needs to have access to the electrical grid and possibly good coverage by mobile networks. Security should also be taken into account - preferably the site should have limited access from both land and sea, and be under some surveillance, which would minimize the risks of equipment damage by people.

Taking into account all these practicalities, we identified two possible options for possible future installation of a monitoring station in the vicinity of the Laboratory of Marine Ecology-Sozopol, as a possible upgrade of the current water quality monitoring program.

Option 1: The ferrybox station can be installed in the building of LME- Sozopol.

Pros: water sampling will be carried out in the same location where the currently ongoing monitoring program is taking place. The servicing and maintenance of the installed equipment will be done in the lab without any logistical difficulties. There will be no issues with security.

Cons: The lab is located on a rocky shore some 20 meters above the sea level. The pumping of water would require the construction of a pump system that can bring water from the sea-level to the lab, which might be difficult in terms of acquiring the necessary permits from the local authorities. Also, during severe sea weather, the site is heavily impacted by storm waves, which could result in possible damage to the pumps and pipe systems.

Option 2: The ferrybox station can be installed in the vicinity of the Border Police harbor in the port of Sozopol.

Pros: The site provides easy access to the sea, the harbor area is just 1-2 m above sea-level, which would make water pumping quite easy and straight forward. The site is secure, it also has access to the electrical grid system and has good mobile network coverage.

Cons: Water sampling will be done in a different location about 1 km away from the current location of water sampling for our monitoring program. Also, the site is possibly under the influence of local waste water discharges from the harbor. Special permits will be needed for the installment of the monitoring station in the area. Additional costs for container installation will be needed too.

Fig. 2 Possible locations for the positioning of a future monitoring station in Sozopol, Bulgaria.

b. Ship-based seasonal sampling with Mini FerryBox system

An alternative to the stationary sampling program is the possible use of the Pocket FerryBox system onboard the small research vessel of LME-Sozopol during the monthly monitoring activities of the lab in the wider Burgas Bay (see https://csr.seadatanet.org/report/21031599). The introduction of the system to our regular monitoring activities would greatly improve the quality and spatial resolution of our monitoring of the eutrophication gradient in the coastal zone of the Burgas Bay. As a first step in this possible future application of the system, we are discussing possible test runs with our partners from Hereon in the framework of other future projects.

Sofia, 15/11/2023

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Location and date Signature of principal investigator