Metrology for marine monitoring: cooperation between INRiM and ENEA

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***Abstract*—The study of the status of the marine environment is typically carried out by monitoring several parameters, both chemical and physicochemical, classified as Essential Ocean Variables by the Global Climate Observing System. These variables are useful to obtain quantifiable indications to monitor the phenomena occurring in the oceans and to relate them to the changes occurring on the global scale in all the environmental compartments. In this framework, a research collaboration is ongoing between the Italian National Metrology Institute (INRiM) and the Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA), to support the collection, validation and maintenance of reliable and accurate databases, by applying the concepts of metrology from the laboratory to the field. Among the main Essential Ocean Variables, the dissolved oxygen and the partial pressure of carbon dioxide are key parameters to monitor the changing ocean and are largely measured in stations around the globe. INRiM and ENEA are collaborating in the measurement of these variables, focusing on the metrological traceability issues and the measurement uncertainty evaluation, also exploiting innovative Internet of Underwater Things (IoUT) in situ monitoring systems developed by WSense, spinoff of Sapienza University.**

Keywords—marine monitoring, metrological traceability, dissolved oxygen, partial pressure of CO_2, Essential Ocean Variables, measurement uncertainty

I. Introduction

The study of the status of the marine environment is typically carried out by monitoring several parameters, both chemical and physicochemical, classified as Essential Ocean Variables (EOVs) by the Global Climate Observing System (GCOS) [1]. These variables are useful to obtain quantifiable indications to monitor the phenomena occurring in the oceans and to relate them to the changes occurring on the global scale in all the environmental compartments. EOVs can be considered key indicators for ocean life and their importance is acknowledged by the entire scientific community and is required to support policy makers and international management in the framework of climate change studies. Another important aspect is the temporal scale at which modifications in the biological systems can be detected, which vary for each EOV and therefore influence the properties being monitored and the length of the time-series.

The observed increase of the levels of carbon dioxide (CO_2) in atmosphere, mainly caused by anthropogenic activities, is also responsible for fundamental changes occurring in the seawater carbonate chemistry. The oceans are absorbing the 25 % of the atmospheric CO_2, which is decreasing seawater pH and leading to the acidification of marine waters, with important consequences for the global ecosystem.

At the same time, the measurement of dissolved oxygen (DO) in the surface layers, due to the exchanges with the atmosphere or deriving from physiological processes of marine organisms, is fundamental for monitoring the state of the ocean and its ecosystems. Ocean deoxygenation is under way in part because of ocean warming and increased stratification, but also because of increased nutrient loads in the coastal ocean [1].

Monitoring the state of oceans and their evolution in space and time is fundamental for their impact on the Earth's global cycle. The oceans are severely impacted by climate change, with observable increase in temperature, acidity and stratification. These variations are responsible for the alteration of the marine ecosystems and for putting many marine species in danger [2, 3].

In this framework, a research collaboration is ongoing between the Italian National Metrology Institute (INRiM) and the Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA - S. Teresa Marine Environment Research Centre) to support the collection, validation and maintenance of reliable and accurate databases, by applying the concepts of metrology from the laboratory to the field.

In this paper, some activities and results related to this joint research collaboration are described. In particular, among the main EOVs, the DO and the partial pressure of CO_2 (pCO_2) are key ocean parameters to be globally monitored. INRiM and ENEA are collaborating in the measurement of these variables, focussing on the metrological traceability issues, the measurement uncertainty evaluation, and the application of Machine Learning (ML) techniques for the study of the trends of several variables in the oceans. The activity also benefits from the deployment in the area of the Smart Bay S. Teresa of an innovative in situ monitoring system designed and managed by WSense which provides in real time every 30 minutes DO, CTD and current data from six points, as part of the EASME SEASTAR project.

II. THE SMART BAY SANTA TERESA

A. Generalities

Santa Teresa Bay (Lerici, Italy) was chosen to host the first Italian Smart Bay, a cooperation platform between research institutions working in the area (ENEA, National Research Council - CNR and National Institute of Geophysics and Volcanology - INGV), local institutions (Municipality of Lerici) and some representatives of small and medium-sized enterprises, working with natural resources within the gulf (Scuola di Mare, Cooperativa Mitilicoltori Associati, WSense through the GREEN STAR project which is a collaboration between the Santa Teresa Bay and the EASME SEASTAR project led by WSense).

Smart Bay Santa Teresa [4] can be considered as a natural laboratory for research, technology, sustainable tourism and mollusc farming. It is the first of its kind in Italy and it is aimed at experimenting with natural resource management strategies, in the coastal marine environment, that have environmental sustainability and blue economy [5] as fundamental points, in accordance with the objectives of the national policies for ecological transition, digitalization and economic recovery [6]. The purpose of this cooperation is to create a completely sustainable and carbon neutral bay [7], which can combine the sustainable use and management of resources and the value of ecosystems and technological development. This initiative is focussed on the marine and terrestrial ecosystems of the Bay (whose functions are studied, also in relation to the ongoing climate change) and the ecosystem services they are able to provide [8].

B. Activities within Smart Bay and collaboration ENEA-INRiM

Smart Bay Santa Teresa develops projects in cooperation with institutes, SMEs and local administrations, for testing new technologies for Ocean Big Data acquisition, for studying marine biodiversity and the ecosystem services provided, all aiming at filling knowledge gap and finding solution to regenerate the marine environment.

Within the purposes of Smart Bay Santa Teresa, ENEA and INRiM recently started to collaborate with the purpose to implement the acquisition and validation of physicochemical marine data on the surface and along the water column in the Bay itself. The data acquired in a multidisciplinary perspective will be analysed and metrologically characterized by ENEA in close collaboration with INRiM (and other partners involved in Smart Bay S. Teresa). The quality control operations of the data acquired in the various measuring stations, as well as being based on the comparison with *in situ* tools (validation in the field), provided by WSense, can also be supported by the application of the ML techniques [9].

The main goals of this collaboration are related both to the support for metrological control and characterization of the acquired data, in terms of uncertainty analysis (with particular focus on the accuracy of pCO_2 measurements) and to the development of procedures for measuring marine physicochemical parameters. The collaboration between ENEA and INRiM is also carried out in the framework of joint research projects, such as the EU MINKE project [10].

Measurements of oceanographic variables such as temperature, pressure, electrical conductivity (and therefore salinity), DO, pH, pCO_2 and seawater currents are nowadays performed in the Bay by means of a monitoring network that consists of 4 fixed stations (or nodes): on each node different probes are installed, at depths ranging from 1 m to 16 m. Some nodes are part of an

“Internet of Underwater Things” (IoUT) system, i.e. they are inter-connected in an (acoustic) submarine wireless network for a real-time acquisition, transmission and visualization of physicochemical data. The system is part of the EASME SEASTAR monitoring infrastructure designed and managed by WSense, spinoff of Sapienza university, deployed in the gulf of La Spezia since 2021, whose accuracy of data has been validated in the GREEN STAR project in collaboration with ENEA by means of periodic sampling and lab validation. An acoustically isolated node, close to Tino Island (figures 1 and 2), supports stand-alone probes, whose data are self-stored and periodically downloaded. In all stations, metrological checks are periodically repeated by means of *ad hoc* ship-based profiles performed with reference probes, together with seawater sampling aimed to further laboratory analysis.

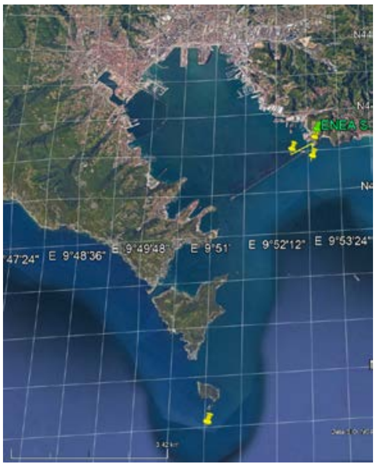


Fig. 1 - Overall view of the Gulf of La Spezia with the four yellow markers indicating the *in situ* monitoring stations providing data to the Smart Bay S. Teresa observatory (the external station is close to the Tino Island, the three nodes close to the area host three of the six monitoring stations deployed by WSense in the gulf of La Spezia).

Fig. 2 - Detail of the three WSense acoustically intercommunicating monitoring nodes, positioned close to S. Teresa bay. The green marker indicates the position of the ENEA Institute.

III. MONITORING OF DISSOLVED OXYGEN IN SMART BAY SANTA TERESA

High resolution monitoring stations and big data production are two of the occurring challenges in ocean studies. In this framework, networks of sensors producing high quality data in real time are becoming a priority. The IoUT technology exploited at Smart Bay Santa Teresa, aims to create a sensor network producing high resolution and quality data for marine ecosystem monitoring. This is based on a WSense [11] wireless sensors network which provides various parameters, such as temperature, oxygen, conductibility for a continuous monitoring. High-cost multi parametric probes such as CTDs and analytical measurements are also employed for IoUT sensor calibration [12].

Within the ENEA-INRiM collaboration, an investigation on the daily variability of the seawater DO with the aim to link its temporal variations with a few environmental parameters such as solar irradiation, air and water temperature is ongoing. The final goal is to forecast the DO content on the basis of the weather forecast only, once time series of a few years are acquired and tested with statistical and ML methods.

The measurement campaign started in December 2021 and data collected until December 2022 were used, with data acquisition every 30 minutes. The oxygen content was monitored and showed to increase due to the phytoplankton production under the solar radiation. In addition, various algae progressively grow over the sensor (an effect named "fouling"), increasing the O_2 daily variability. This is due to the fact that no wiper or automatic sensor cleaning or other methodologies to limit biofouling were used in the experiments performed in the relevant timeframe. To limit the fouling, the sensors were manually cleaned every 8-10 days.

The first work carried out at INRiM, was to decompose the measured signal into a daily component (the *Seasonal* one in time series analysis) and a *Trend* component, taking into account long time variations purged from the fouling effects. After performing this decomposition on a preliminary series of data, the daily means of a few parameters were used to train a random forest algorithm for O_2 prediction. It resulted that only solar radiation, and the water and air temperatures actually affected the regression reconstruction. Future investigations will include different methods of decomposition, and analysis of the time signal with recurrent neural networks.

IV. MONITORING OF *p*CO_2

In the field of CO_2 monitoring, INRiM, being the Italian National Metrology Institute, contributes to assure metrological traceability to these measurement results. In the marine sector, the capabilities developed at INRiM, both in terms of reference material production and analytical verification, can support the metrological framework for *p*CO_2 monitoring. In particular, INRiM is working on the production of gaseous certified reference materials (CRMs) for amount of substance fraction of CO_2, and to investigate their applicability for the calibration and verification, also *in situ*, of the *p*CO_2 analysers.

The CRMs are produced by means of a primary method, the gravimetry, and this procedure is defined in [13]. The gravimetric method consists in the preparation of binary or multicomponent gas mixtures, by weighing and mixing known masses of gases, and to determine the amount fraction of the components in the final mixture on the basis of these masses, determined by a high precision weighing. This step is carried out by using a mass comparator, which allows the weighing of the cylinder in preparation with respect to a reference cylinder, thus obtaining very low preparation uncertainties.

Fig. 3 - Detail of the mass comparator used at INRiM for the gravimetric preparation of reference gas mixtures.

In addition to the CRM preparation, another activity carried out at INRiM is represented by the analytical certification of CO_2 in nitrogen or synthetic air mixtures, by verifying their composition with selective analysers, such as the Non-Dispersive Infrared (NDIR) photometers. The NDIR technique is reliable, robust and widely applied for laboratory measurements and for *in situ* monitoring of the atmospheric CO_2. NDIR analysers are also applied for the monitoring of *p*CO_2, measuring the CO_2 extracted from aqueous samples in dedicated systems that allow the equilibration of the liquid and gaseous phase of the samples under study.

The verification and certification of the composition of different CO_2 in air mixtures in the amount fraction range (300-900) μmol mol^{-1}, is carried out at INRiM, to assure the proper calibration and periodic verification of NDIR analysers, which can be mounted on ships for *in situ* sampling and measurement of *p*CO_2. An example of this activity is the recent collaboration with the team of the trimaran Maserati Multi70, led by Giovanni Soldini. Some analysers are mounted on the trimaran, in the multi-parametric monitoring system *OceanPack – RACE*, produced by subCtech. The system acquires physicochemical data such as temperature, salinity, O_2 and *p*CO_2 (sampling depth 1 m) along the route of the trimaran and contributes to the collection of data during the navigation also in remote areas [14]. The seawater *p*CO_2 sensor mounted on the trimaran was calibrated by means of CO_2 mixtures certified at INRiM and its performances were compared in field with a proper sensor, by ENEA S. Teresa. Some of the obtained data are presented in the following section.

V. RESULTS AND DISCUSSION

At ENEA, a CO_2-Pro CV probe (Pro-Oceanus Systems Inc., Canada), shown in Fig. 4, is currently used for measuring the CO_2 concentration in seawater.

Fig. 4 - CO_2-Pro CV probe on bench.

The probe has the following characteristics:

- Range 0-2000 ppm;
- Maximum depth 600 m;
- Accuracy, as declared by the manufacturer, equal to ±0.5 % of the maximum range (i.e. 10 ppm).

In addition to the factory calibration, periodically and before each use, the probe is checked at ENEA by measuring a mixture of known CO_2 concentration, flushed in air at ambient pressure for about half an hour. During the last metrological check, a mixture with a CO_2 concentration value of (447.8 ± 2.2) ppm was used; the mean concentration measured by the probe was equal to (445.5 ± 6.2) ppm, where the reported standard uncertainty was calculated by combining the contributions of the declared accuracy term and the measured repeatability, respectively. As a result, the metrological check was found to be reasonably verified. As an example of use in the field, as part of the Smart Bay Santa Teresa activities, the CO_2-Pro CV probe was employed to perform a preliminary metrological check of the *OceanPack-RACE* measurement system, at the time just mounted on the trimaran Maserati Multi70 (see paragraph IV). The opportunity to carry out this verification took place on 27 May 2022, just before the first campaign of the *OceanPack-RACE*; the CO_2-Pro CV was deployed at the pier in the bay of S. Teresa, at a depth of 1 m and about 10 m far from the *OceanPack-RACE* probe mounted on the trimaran. In Fig. 5 the trimaran Maserati Multi70 is shown.

Fig. 5 - Trimaran Maserati Multi70 approaching the pier in S. Teresa Bay.

After respecting the stabilization times of both the instruments, at least half an hour, the pCO_2 values were acquired for about twenty minutes at sampling rates of 1 measure every 10 s for *OceanPack-RACE* and every 1 s for CO_2-Pro CV, respectively. Results of this comparison, in terms of measured mean concentrations, calculated respectively on 119 and 1169 samples, were as follows:

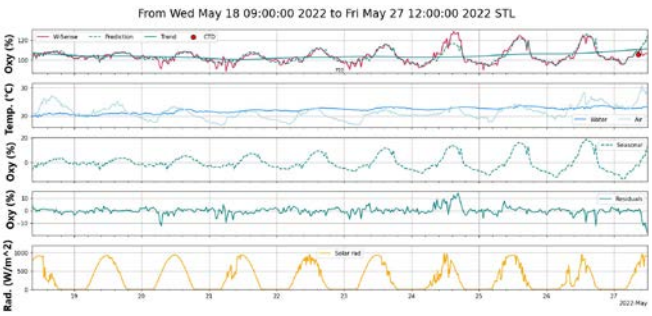
- pCO_2 (*OceanPack-RACE*) = (485 ± 35) ppm, where the standard uncertainty was calculated as the standard dispersion of the measures (as an estimate of the measurement reproducibility);

- pCO_2 (CO_2-Pro CV) = (471 ± 7) ppm, where the standard uncertainty was calculated by combining the measurement reproducibility with the result of the check performed with the calibrated gas mixture.

Even if the measurements obtained appear reasonably comparable, thanks to the overlapping of their uncertainty bands, it should be underlined that the dispersion of the *OceanPack-RACE* values, under the assumption that the seawater sample is reasonably stable in the period considered, is quite high compared to the specifications declared by the manufacturer (accuracy of ±0.5 ppm under calibration condition). First, thanks to this experiment, it has been discovered that this fact is essentially due to an actual drift of the signal of about 3 hours, following the switch-on of the instrument, which will have to be carefully taken into account in its subsequent use, before steady state measurements can be acquired. As a second result, the need for a general metrological revision of this instrument by the manufacturer was highlighted. This was just one example of the application of the facilities offered in the field by Smart Bay Santa Teresa.

As concerns the seawater DO, an analysis of data collected over 260 days (Dec 2021 - Dec 2022) was performed [15]. Figure 6 shows a typical week (18-27 May 2022) of data collection and elaboration. The data were acquired every 30 minutes.

Fig. 6 - Decomposition of the oxygen content in % (red curve) with Trend (solid green line), Seasonal and Residuals. Temperatures of water and air in blue and solar radiation in gold. CTD sensor value for calibration is the red dot.



The quantity of interest was the measured oxygen percentage (red curve in figure 6), with the corresponding thermodynamic value of the O_2, calculated at the measured water temperature and salinity, taken as the reference 100 % value. The O_2 content increased during the day, due to the phytoplankton production under the solar radiation, and decreased by night. Moreover, these daily fluctuations progressively increased in amplitude, due to the growing of algae over the sensor (fouling effect). This happened especially in spring and summer time, when temperature was higher. To tackle this complex combination of variability effects, the "Seasonal-Trend decomposition using LOESS" (STL) method [16] was applied to analyse the time series, since this method is robust to outliers and allows for a non-constant seasonal component (the daily variation, in this case, that increases in time). After decomposing the time series variations, the daily means of the following parameters were used to apply a ML model: the mean trend of the O_2, the mean and the standard deviation of the air and water temperatures, and the mean solar radiation. A random forest (RF) model was trained to estimate the O_2 content based on the air and water temperatures, the solar radiation and the number of days passed from the last cleaning, as input parameters to the ML model. Once properly renormalized, 90 % of the data were used to train the RF, and 10 % for test, chosen randomly. It interestingly resulted that the standard deviation of water and air temperatures, together with the number of days between successive cleanings, were completely irrelevant in the regression, whereas the solar radiation weighted for about 60 %, and the water and air temperatures (mean values) for 20 % each. Remarkably, the O_2 prediction were accurate within about 4 %.

VI. CONCLUSIONS

In the present paper, two examples of collaboration between the Italian National Metrology Institute and ENEA Marine Research Centre S. Teresa were presented. In particular, the ongoing collaboration devoted to the measurement of some EOVs, such as DO and $p\mathrm{CO}_2$ as a starting point, will contribute significantly to spread and apply the pillars of metrology in this particular field of marine monitoring.

In particular, for DO, the investigation of the possibilities of emerging ML techniques will open the path for a deeper understanding of the trends of this parameter in the oceans, and of the possible interfering variables in the measurement process *in situ*. This activity benefits from the possibility to gather large amounts of data from the water column thanks to innovative IoUT *in situ* monitoring systems developed by Sapienza's spinoff WSense. Another long-term goal would be the forecasting of the seawater O_2 content only on the base of the weather parameters forecast.

As for $p\mathrm{CO}_2$, the possibility to apply on a larger scale the measurement approaches and reference materials already used in the gas-monitoring field will help to homogenise the measurement procedures and consolidate the metrological traceability in this field.

The cooperation between the two Institutions will be also fruitful within the participation in European and International research projects, such as the ongoing H2020 MINKE project, as well as in supporting the S4SEA project, between Smart Bay S. Teresa and Giovanni Soldini, aiming to validate and analyse physicochemical parameters acquired via the *OceanPack – RACE* system, mounted on the trimaran Maserati Multi70.

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