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Joint European Research Infrastructure for Coastal Observatories Science, Services, Sustainability

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TABLE OF CONTENTS

TABLE OF CONTENTS	3
1. EXECUTIVE SUMMARY	5
2. INTRODUCTION	5
3. MAIN REPORT	6
3.1. Biogeochemical variables observed in near real-time by JERICO-RI	6
3.1.1. Dissolved oxygen	6
3.1.2. Carbonate system chemistry	8
3.1.3. Coloured dissolved organic matter	9
3.1.4. Inorganic nutrients	12
3.2. General considerations for near real-time data quality control of biogeochemical data	16
3.3. Examples of near real-time multiplatform biogeochemical observations within JERICO-S3	17
3.3.1. Example 1: Dissolved oxygen and chl a from buoy, glider, and research vessels in the Western Mediterranean Sea (SOCIB)	18
3.3.2. Example 2: Coloured dissolved organic matter, chl a, carbonate chemistry from FerryBoxes and research vessels along the Norwegian coast (NIVA)	19
3.3.3. Example 3: Carbonate chemistry from a fixed platform and research cruises in the Adriatic Sea (CNR)	22
3.3.4. Example 4: Carbonate chemistry observations from satellites, research vessels, fixed platform, and an atmospheric station (HCMR)	25
3.3.5. Example 5: Carbonate chemistry observations from fixed platforms and research vessels in the Northwest Mediterranean Sea (CNRS)	28
3.4. Recommendations for near real-time biogeochemical observations	30
4. CONCLUSIONS	31

List of abbreviations

AT: Total alkalinity

BGC: Biogeochemical

CDOM: Coloured dissolved organic matter

CMEMS: Copernicus Marine Environment Monitoring Services

CO₂: Carbon dioxide

CO₃²⁻: Carbonate

CT: Total dissolved inorganic carbon

CTD: Conductivity, Temperature, Depth

DO: Dissolved oxygen

DOC: Dissolved organic carbon

DOM: Dissolved organic matter

EEM: Excitation emission matrix

EOVs: Essential Ocean Variables

fDOM: Fluorescent dissolved organic matter

HCB: Heraklion Coastal Buoy

HCO₃⁻: Bicarbonate

IC: Ibiza Channel

ICOS-RI: Integrated Carbon Observing System-Research Infrastructure

ILICO-RI: French Research Infrastructure for Coastal Ocean and Nearshore Observations

IRS: Integrated Regional Sites

ISFET: Ion-sensitive field-effect transistor

JERICO-RI: Joint European Research Infrastructure of Coastal Observatories-Research Infrastructure

JERICO-S3: Joint European Research Infrastructure of Coastal Observatories: Science, Service, Sustainability

LED: Light Emitting Diode

LoC: Lab on a chip

MC: Mallorca Channels

NCP: Net Community Production

NDIR: Nondispersive infrared

pCO₂: Partial pressure of carbon dioxide

PSS: Pilot Supersites

RTQC: Real time quality control

SOCAT: Surface Ocean CO₂ Atlas

SOLAS: Surface Ocean - Lower Atmosphere Study

SSS: Sea surface salinity

QC: Quality control

UV: Ultraviolet

1. EXECUTIVE SUMMARY

This Deliverable provides recommendations for multiplatform implementation of near real-time biogeochemical observations within the JERICO-S3 coastal observing framework. Near real-time sensor-based observations of the biogeochemical Essential Ocean Variables (EOVs) – dissolved oxygen, inorganic carbon, dissolved organic matter, and nutrients – are described in the first section of the Main Report. This is followed by five examples from JERICO-S3 Integrated Regional Sites (IRS) and Pilot Supersites (PSS) where multiplatform biogeochemical observations have been carried out, and how multiplatform observations have been performed. The main recommendations, due in part to the high degree of difficulty in making high quality biogeochemical observations, include utilising a well-constrained (near) real-time quality control (QC) system informed by existing datasets and model outputs, validate/compare observations made by complementary observing platforms (including other autonomous platforms, remote sensing products, etc.; i.e., multiplatform approach), and finally validation via traditional oceanographic (research vessel-based) sampling and laboratory analytical techniques.

2. INTRODUCTION

Biogeochemical observations are a crucial component of JERICO-S3 coastal observing efforts. These include the measurement of essential ocean variables (EOVs) such as dissolved oxygen, inorganic carbon, dissolved organic matter, and nutrients, among others. The observations of these variables link physical processes (e.g., circulation and upwelling) to biological processes (e.g., photosynthesis and respiration) to chemical cycling of bioactive elements (e.g., carbon, nitrogen, phosphorus). While traditional water sampling and analysis in the laboratory is routine for biogeochemical variables, sensors for biogeochemical observations are generally less mature and less robust than standard oceanographic sensors. In part, biogeochemical EOVs measurements present a high degree of difficulty compared to physical EOVs, for example. Careful calibration of these sensors increases the quality of observations, and comparison to other observing platforms across space and time provides valuable validation of consistency.

Therefore, this Deliverable covers the topic of multiplatform observations of biogeochemical variables within the JERICO-S3 research infrastructure. This includes a brief description of measurements within JERICO-S3 Integrated Regional Sites (IRS) and Pilot Supersites (PSS) that align with biogeochemical EOVs - dissolved oxygen, carbonate chemistry, coloured dissolved organic matter, and nutrients. This is followed up with a subsection on near real-time data quality control recommendations. Then five examples of multiplatform biogeochemical observations are provided from the Iberian Atlantic Margin-IRS, Norwegian Sea-IRS, Northern Adriatic-IRS, Cretan Sea-PSS, and the North-western Mediterranean-PSS. The final section of the Main Report compiles recommendations for future multiplatform implementation of near real-time biogeochemical observations.

3. MAIN REPORT

3.1. Biogeochemical variables observed in near real-time by JERICO-RI

The following subsections details knowledge to date pertaining to biogeochemical EOVS, sensors and/or sensor types that are available for deployment on ocean observing platforms for near real-time data collection, and performance/calibration considerations for operational use.

3.1.1. Dissolved oxygen

Dissolved oxygen (DO) concentrations are the product of a complex equilibrium between exchanges at the ocean-atmosphere, thermodynamic solubility equilibrium and biological fluxes (photosynthesis and respiration) in the water column. The variations of DO concentrations integrate all these phenomena. Thus, an accurate description of the dynamics of the oceanic dissolved oxygen content based on a coastal observing system can help to answer to: the spreading of oxygen minimum and to predict hypoxia and anoxia events, the estimation of Net Community Production (NCP) used in the carbon pump context, the estimation of anthropogenic CO₂ based on carbonates variables and nutrients concentrations and the exchanges at the sediment-water interface.

Two groups of sensors are used in oceanography. The electrochemical sensors which are based on the Clark cell. In this cell, DO diffuses through a membrane (permeable to gas) in contact with the sea water and undergoes an amperometric reduction. The cathodic current measured is proportional to the diffusive flow of oxygen at the electrode and can be related to the concentration of dissolved oxygen in solution.

The optical sensors (or optodes) which are based on the quenching of the luminescence emitted by a luminophore immobilised on a sensitive membrane (a platinum-porphyrin complex on a silicone matrix). By quenching effect, oxygen reduces the lifetime of luminescence emitted by this luminophore excited by a light pulse. In the optodes, the phosphor is excited by a wavy light generated by a blue light emitting diode (LED). The luminescence quenching induces a phase difference in the luminescent response of the membrane. A reference phase reading is taken by a red LED. Thus, the phase difference between the reference radiation and the luminescence of the membrane is related to the amount of oxygen diffusing into the membrane. In contact with seawater, the optodes can therefore estimate the concentration of dissolved oxygen.

These two groups of sensors have advantages and disadvantages that justify their implementation:

1. The electrochemical sensors developed for several decades are accurate and have short response times. They are routinely used during bathysonde profiles during oceanographic campaigns. The SBE43 sensor developed by Sea-Bird Scientific (www.seabird.com) is used in many CTD-rosette casts. However, this sensor drifts strongly over time (e.g., biofouling effect) and has a high energy consumption, limiting its use on autonomous platforms.
2. Optodes have been developed for in-water applications for about two decades and commercial sensors for measurements along the water column have been available for more than 10 years now (Aanderaa: www.aanderaa.com, Sea-Bird, JFE: <https://www.jfe->

advantech.co.jp/eng/, NKE: nke-instrumentation.com, and others). Due to their size, low power consumption and a priori good stability of the measurement over time¹, optode type sensors are widely used on autonomous platforms (e.g., glider, Argo float, instrumented mooring).

The performance of these sensors has greatly increased in recent years, yet the accuracy of DO measurements is still not optimal due to the large number of sources of uncertainty. For example, in addition to the strong drift over time of electrochemical sensors, these two groups of sensors present a quasi-systematic bias during their deployment even if they have been correctly calibrated by the suppliers. This phenomenon is certainly largely related to the ageing of the membranes. It is therefore necessary to apply systematic corrections of this bias.

In this context, the Argo-O₂ community has shown a certain dynamism in recent years for the validation/correction of dissolved oxygen data acquired on floats from optodes². Recent studies have shown that measuring the partial pressure of oxygen in air by the optode when the float is at the surface allows to correct the drift of DO measurements and to obtain results with an accuracy of 1%^{3,4}. This method of correcting oxygen data using Argo floats⁵ could be potentially used on gliders, provide new possibilities for surface drones, or other observing platforms. For coastal buoys and moorings, the reference method recommended is the regular measurements of in situ DO by Winkler techniques, still considered as the reference method. In this case, a slope correction can be applied on pO₂ values⁵. For gliders, if measurements in the air are not feasible due to the mounting of the sensor on the glider, a regular comparison of the optode values with the Winkler measurements during the glider's trajectory is strongly recommended, of course provided that the glider passes over waypoints where in situ measurements are regularly performed⁶.

The most common and recommended DO optodes for autonomous platforms are Aanderaa 4330, SBE63 from Sea-Bird Scientific and more recently the RINKOIII (buoy/mooring) or AROD-FT (gliders, Argo) from JFE.

The calibration of optode 4330 and SBE63, performed by manufacturers, has been enhanced toward a multi-point calibration procedure (35 points) to provide the best sensor accuracy.

¹ Körtzinger, A., Schimanski, J., and Send, U. (2005). High quality oxygen measurements from profiling floats: a promising new technique. *J. Atmos. Oceanic Technol.* 22, 302–308. doi: 10.1175/JTECH1701.1

² Thierry, V., Bittig, H., Gilbert, D., Kobayashi, T., Kanako, S., and Schmid, C. (2018). Processing Argo Oxygen Data at the DAC level, v2.3.1. doi: 10.13155/39795

³ Johnson, K. S., Plant, J. N., Riser, S. C., and Gilbert, D. (2015). Air oxygen calibration of oxygen optodes on a profiling float array. *J. Atmos. Oceanic Technol.* 32, 2160–2172. doi: 10.1175/JTECH-D-15-0101.1

⁴ Bittig, H. C., and Körtzinger, A. (2015). Tackling oxygen optode drift: near-surface and in-air oxygen optode measurements on a float provide an accurate in situ reference. *J. Atmos. Oceanic Technol.* 32, 1536–1543. doi: 10.1175/JTECH-D-14-00162.1

⁵ Bittig, H. C., Körtzinger, A., Neill, C., van Ooijen, E., Plant, J. N., Hahn, J., et al. (2018). Oxygen optode sensors: principle, characterization, calibration, and application in the ocean. *Front. Mar. Sci.* 4:429. doi: 10.3389/fmars.2017.00429

⁶ López-García, P., Hull, T., Thomsen, S., Hahn, J., Queste, B.Y., et al (2022) OceanGliders Oxygen SOP, Version 1.0.0. OceanGliders, 55pp. <http://dx.doi.org/10.25607/OBP-1756>.

For these optodes, a data processing and qualification chain has been defined in a best practices manual² and a guide has been written for the mounting of sensors on Argo platforms to enable in-air sampling⁴. For the optodes, they observed a strong DO sensitivity drift exists (order -5% per year between calibration and deployment) even after multi-points calibration, which should be corrected with a factor on the pO_2 . This “storage drift” can be easily estimated during the platform deployment when in situ sampling is performed or during in air measurements. Secondly, a smaller “in situ drift” can occur during the sensor deployment (-0.5% per year) and it could be estimated during regular calibrated CTD-O2 profiles near the sensor deployment. Regarding the RINKO optodes, JFE applies a two-points calibration method (0-100% saturation) for RINKOIII and the multi-point procedure for AROD-FT sensor (15 points) which should be sufficient to measure DO variability in coastal waters. Several analyses are underway for the application of this type of optode in oceanography and it is obvious that other user guides on these optodes will appear soon.

3.1.2. Carbonate system chemistry

Carbon (C) is a basic building block for life on earth. In the oceans, C enters the food web primarily via inorganic C uptake and C fixation through photosynthesis by primary producers such as microalgae (or phytoplankton) and macroalgae. Inorganic C consists of three species: carbon dioxide (CO_2), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}). While the RuBisCo enzyme that facilitates photosynthesis requires CO_2 as its primary substrate, most oceanic primary producers can also utilise other forms of inorganic C including HCO_3^- through various carbon concentrating mechanisms. Inorganic C is also used by e.g., some types of phytoplankton, bivalves, and corals to form calcareous structures. Biomineralization of calcareous structures can use both HCO_3^- and CO_3^{2-} in addition to calcium to form aragonite and calcite. The saturation state of aragonite and calcite (Ω_{Ar} and Ω_{Ca} , respectively), or the level at which dissolution of these calcareous forms is chemically favoured (or unfavoured), can be estimated based on carbonate system measurements (in addition to salinity and temperature).

At present, the main carbonate system variables that are measurable using laboratory instruments include total dissolved inorganic C (CT; the sum of the three inorganic C species), total alkalinity (AT; the sum of proton acceptors in seawater), pCO_2 , and pH (the concentration of protons in seawater). A recent technique has been used to measure CO_3^{2-} ion via spectrophotometry, but generally not yet widely in use. With measurements of salinity, temperature, pressure, phosphate and silicic acid (although negligible at low concentrations), and any two of the four above-mentioned carbonate system variables (CT, AT, pCO_2 , or pH), the remaining carbonate system variables including Ω_{Ar} and Ω_{Ca} can be calculated using software such as CO2SYS⁷ or seacarb⁸.

For near real-time measurements on JERICO-RI ocean observing platforms, the majority of measurements are presently being made for pCO_2 and pH (some sensors for AT measurements are available, but not widely used at this time). Sensors presently employed for pCO_2 measurements include membrane equilibrators sensors with near infrared detectors

⁷ <https://www.ncei.noaa.gov/access/ocean-carbon-acidification-data-system/oceans/CO2SYS/co2rprt.html>

⁸ van Heuven, S., D. Pierrot, J.W.B. Rae, E. Lewis, and D.W.R. Wallace. 2011. MATLAB Program Developed for CO2 System Calculations. ORNL/CDIAC-105b

(NDIR) that are either flow-through (seawater pumped across a gas permeable membrane) or in situ (sensor and gas permeable membrane submerged in seawater). There are also shower-head equilibrators systems (CO₂ equilibrated between droplets of seawater and air in an equilibration chamber) equipped with NDIR detectors also in use within JERICO-RI and also with ICOS-RI. Sensors for pH measurements include flow-through colorimetric techniques via spectrophotometric detection (using pH sensitive reagents such as meta-cresol purple, thymol blue, bromocresol green) and ISFET pH electrodes (ion-sensitive field-effective transistor). Standard operating procedures and calibration techniques (using certified reference materials: seawater and Tris buffers) are primarily covered in Dickson et al. (2007)⁹.

Sensors for pCO₂ and pH have been deployed on various JERICO-RI observing platforms. Flow-through pCO₂ sensors are primarily deployed on FerryBoxes and fixed stations, while in situ membrane-based pCO₂ sensors are primarily deployed on glider, Argo floats, and mooring/buoy systems and seafloor installations. Membrane pCO₂ equilibrators are most widely used due to smaller physical footprints and lower costs. Flow-through spectrophotometric pH sensors are primarily deployed on FerryBoxes as well as some use on mooring/buoy systems, while ISFET pH electrodes are in use on a wide variety of observing platforms including FerryBoxes, mooring/buoy systems, floats, gliders, mooring/buoy systems, and seafloor installations. Sensor-based pCO₂ and pH measurements are often coupled with CT and AT analysis of discrete samples collected from/near observing platforms and from conventional research cruises using CTD rosette systems.

3.1.3. Coloured dissolved organic matter

By definition, marine dissolved organic matter (DOM) is the fraction of organic matter that passes through a 0.2-0.7 µm filter. It consists of various organic compounds, either produced within the marine aquatic system (autochthonous) or originating from terrestrial systems (allochthonous) including also human-made compounds. Main loss processes of DOM are photodegradation especially due to UV light, microbial degradation, and aggregation along fresh water – ocean gradient. Marine DOM includes a wide range of different compounds and depending on the origin of DOM and the state of degradation, its chemical, physical, and optical characteristics vary a lot^{10,11}.

Marine dissolved organic carbon (DOC), i.e., carbon that DOM contains, is one of the largest pools of organic carbon on Earth. DOM provides a significant source of carbon and nutrients to marine microbes. The coloured fraction of DOM (coloured dissolved organic matter, CDOM) absorbs light, especially in the UV range and it influences heat budgets and stratification of water bodies as well as light penetration. The increase of DOM loads by rivers

⁹ Dickson A.G., Sabine C.L. & Christian J.R. (2007) Guide to best practices for ocean CO₂ measurements, North Pacific Marine Science Organization.

¹⁰ Coble P, Lead J, Baker A, Reynolds D, Spencer R. (Eds.). (2014). Aquatic Organic Matter Fluorescence (Cambridge Environmental Chemistry Series). Cambridge: Cambridge University Press. doi:10.1017/CBO9781139045452

¹¹ Lønborg C, Carreira C, Jickells T, Álvarez-Salgado XA (2020) Impacts of Global Change on Ocean Dissolved Organic Carbon (DOC) Cycling. Front. Mar. Sci. 7:466. doi: 10.3389/fmars.2020.00466

is causing brownification, intensification of water colour, and also affecting the balance between autotrophy and heterotrophy of recipient waters¹⁰.

Overall, DOM and DOC are important determinants of water quality locally and significant components in global carbon cycling. Their spatio-temporal distribution patterns, trends and dynamics are therefore actively monitored. While analytical determination of DOM and DOC from water samples requires various steps in laboratory and dedicated bench-top instruments, optical properties of DOM can be used as proxies of the amount and quality of DOC and DOM.

CDOM absorbs efficiently in the UV and blue regions of the spectrum. CDOM can be most reliably measured from filtered water samples, providing spectral absorption coefficients of CDOM, with units m^{-1} . Absorption coefficient at some specific wavelengths (e.g., 335, 412 or 443 nm) is often considered as proxy for concentration of DOM or DOC, though there is considerable variability in DOC-specific absorption. Slope factor, characterising the exponential shape of absorption spectra, is used as an indicator of the origin or age of CDOM^{12,13}.

Some online measuring systems for CDOM absorption are available, based of liquid waveguide capillary cells (e.g., UPUV-2 from World Precision Instrument: <https://www.wpi-europe.com/products/spectroscopy/optical-detection-systems/upuv-2.aspx>), integrated cavity absorption (e.g., OSCAR from TRIOS GmbH: <https://www.trios.de/en/oscar.html>), or technologies based on combined absorption and attenuation measurements (e.g., AC-9 or AC-s from Sea-Bird Scientific). When using these technologies, an additional filtration step, to separate CDOM from signals of those of particulate matter, can be constructed. Alternatively, spectral analysis can be used to decompose contributions of various optically active compounds, like CDOM. Some of these systems are typically for benchtop use only (especially liquid waveguide capillary cells), limiting their continuous and automated use for research cruises and flow through systems of FerryBoxes and fixed platforms. Integrated cavity absorption systems and absorption/attenuation meters can be used in profiling mode as well. However, CDOM absorption measurement is very sensitive to all kinds of fouling, and therefore frequent cleaning of measuring cells and cuvettes need to be carried out, limiting the use of such systems for long term deployments. To further respond to fouling and shifts in measuring systems in general, frequent calibrations need to be conducted, and high-quality pure water (and some calibrants) need to be available. Thus, often the use of CDOM absorption sensors is limited to specific cruises, or flow through systems and unattended long-term deployments are rare¹⁴.

¹² Twardowski MS, Boss E, Sullivan JM, Donaghay PL (2004) Modeling the spectral shape of absorption by chromophoric dissolved organic matter. *Marine Chemistry* 89, 1–4, p. 69-88

¹³ Sosik H, (2008). Characterizing seawater constituents from optical properties, in: Babin M et al. (Ed.) *Real-time coastal observing systems for marine ecosystem dynamics and harmful algal blooms: Theory, instrumentation and modelling*. Oceanographic Methodology Series, pp. 281-329

¹⁴ Mannino A, Novak MG, Nelson NB, Belz M, Berthon J- F, Blough NV, Boss E, Bricaud A, Chaves J, Del Castillo C, Del Vecchio R, D'Sa EJ, Freeman S, Matsuoka A, Miller RL, Neeley AR, Röttgers R, Tzortziou M, Werdell PJ (2019) Measurement protocol of absorption by chromophoric dissolved organic matter (CDOM) and other dissolved materials, In *Inherent Optical Property Measurements and Protocols: Absorption Coefficient*, Mannino, A. and Novak, M. G. (eds.), IOCCG Ocean Optics and Biogeochemistry Protocols for Satellite Ocean Colour Sensor Validation, Volume ###, IOCCG, Dartmouth, NS, Canada. <https://ioccg.org/wp->

CDOM is composed of various coloured compounds, many of which are fluorescent, and called as fluorescent DOM (fDOM). Overall fDOM fluorescence intensity can be measured with specific pre-selected waveband combinations of excitation and emission, matching some of the main fluorescence compounds. Fluorescence intensity, often represented in the units of quinine sulphate equivalents commonly used for sensor calibration, is considered as a proxy of CDOM or DOC. The relationship between fDOM and CDOM absorption or DOC concentration shows quite some variability due to the origin of DOC/CDOM and also due to fluorescence wavebands used. fDOM fluorescence probes use principally the same technology as chlorophyll fluorometers and typically their housings are identical. Therefore, fDOM sensors can be easily deployed in most platforms, like gliders, buoys, profilers, FerryBoxes and fixed platforms. As fluorescence of fDOM is temperature dependent, temperature correction should be carried out prior to the use of the data⁹.

Wavelengths of fDOM probes vary, depending on manufacturer and the key target fluorescent compound(s). Some sensors aim to measure natural DOM while some use wavebands specific for contaminants like oils and PAH compounds. As signals of DOM and contaminants may be slightly overlapped, it is beneficial to combine detection of contaminants with DOM sensors, to screen for false positives in detection of contaminants due to increased DOM levels.

fDOM wavelength dependency varies depending on the quality of DOM and is characterised by fluorescence excitation emission matrix (EEM), a measurement done covering all wavelengths of excitation and emission where fDOM shows fluorescence. Therefore, measuring whole EEM recovers information on the main fluorescent organic compounds, like humic-like tyrosine-like and tryptophan-like components, and their contributions can be mathematically sorted out¹⁵. There have been some demonstrations of flowthrough measuring systems for fDOM EEMs¹⁶, but mostly the EEMs are measured in the laboratory from discrete samples. Some new sensors take the advancements of EEM and include several wavebands for fDOM detection (e.g., UviLux from Chelsea Technologies Ltd: <https://chelsea.co.uk/products/uvilux-tryptophan-sensor/>; and matrixFlu from TRIOS GmbH: <https://www.trios.de/en/matrixflu-vis.html>) and they are better aimed to detection of various fDOM components simultaneously, compared to single waveband sensors. The multiwavelength sensors are also applicable to all platforms, due to their overall small size and low power consumption. In addition, LIDARs have been used in detection of bulk fDOM or spectral variability of fDOM, and for detection of oils and Polycyclic Aromatic Hydrocarbons (PAHs). These systems are often large and available only for above-surface sensing, e.g., ships and fixed platforms.

content/uploads/2019/10/cdom_abs_protocol_public_draft-19oct-2019-sm.pdf (accessed 23.01.2023)

¹⁵ Fellman JB, Hood E, Spencer RGM (2010). Fluorescence spectroscopy opens new windows into dissolved organic matter dynamics in freshwater ecosystems: A review. *Limnol. Oceanogr.*, 55, 2452–2462.

¹⁶ Babichenko S, Leebein A, Poryvkina L, van der Weert R, de Vos F (2000) Fluorescent screening of phytoplankton and organic compounds in sea water. *J Env Monit* 2: 378-383

3.1.4. Inorganic nutrients

Although nutrients are essential to marine life, their inputs from rivers to open ocean have been intensified with the enhancement of agricultural practices and population growth. These inputs have induced the decrease in water quality in many estuaries and coastal seawaters (eutrophication, nuisance, harmful algal blooms, etc.). Thus, determining the dynamics of nutrients in seawater is capital. Strong concentration gradients are typically observed from estuarine, coastal and open ocean waters¹⁷. They also appear vertically in the seawater column (e.g., biological uptake, remineralization, upwelling)¹⁸. Moreover, episodic and transient events such as phytoplankton blooms, storms, runoff, wastewater treatment discharges modify the distribution of nutrients in seawater. That is why high temporal and spatial resolution measurements are required to characterise such events. In situ nutrient sensors have been identified as relevant tools across the marine community to enhance the resolution of nutrient profiles in finer detail¹⁹. This is particularly true when good practices derived from laboratory reference methods are applied²⁰.

At present, three main analytical technologies have been used for *in situ* nutrient monitoring: wet chemical, optical, and electrochemistry systems. It should be noted that rarely is a single sensor type suitable for all deployment purposes, applications, platforms or monitoring strategies, but there are sensors whose characteristics are specific to a particular type of deployment. Figure 1 (from Daniel et al., 2020²⁰) displays the spatial and temporal coverage of the platforms and dedicated in situ sensors.

¹⁷ Zhang, J., Liu, S.M., Ren, J.L., Wu, Y., Zhang, G.L., 2007. Nutrient gradients from the eutrophic Changjiang (Yangtze River) Estuary to the oligotrophic Kuroshio waters and re-evaluation of budgets for the East China Sea Shelf. *Prog. Oceanogr.* 74, 449–478.
<https://doi.org/10.1016/j.pocean.2007.04.019>

¹⁸ Sigman, D.M., Hain, M.P., 2012. The Biological Productivity of the Ocean: (1) What is Ocean Productivity? *Nat. Educ.* 3, 1–16.

¹⁹ Prien, R.D., 2007. The future of chemical in situ sensors. *Mar. Chem.* 107, 422–432.
<https://doi.org/10.1016/j.marchem.2007.01.014>

²⁰ Daniel, A., Laës-huon, A., Barus, C., Beaton, A.D., Blandfort, D., Guigues, N., Knockaert, M., Muraron, D., 2020. Toward a Harmonization for Using in situ Nutrient Sensors in the Marine Environment 6, 1–22. <https://doi.org/10.3389/fmars.2019.00773>

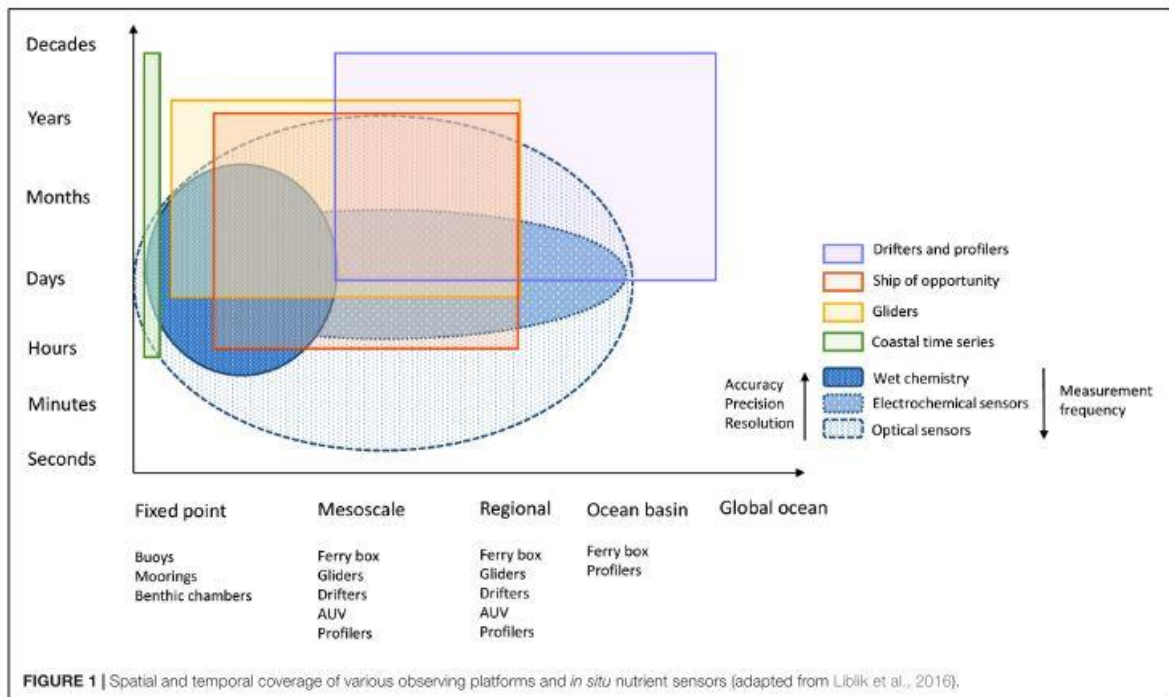


Figure 1. Spatial and temporal coverage of various observing platforms and *in situ* nutrient sensors (from Daniel et al., 2020²⁰).

The basic analytical principles for most of the *in situ* wet chemical analyzers are derived from standard colorimetric analytical methods, which use chemicals either to form a coloured reaction product which is then detected spectroscopically, or by using a fluorescence analytical technique. These *in situ* analytical instruments are usually based on FIA (Flow Injection Analysis) or on batch analysis. Many instruments based on flow injection analysis (FIA) (Table 1) have been developed and used by academic institutions. Miniaturisation of the manifold sensors has been a focus over recent years with the development of sensors based on microfluidics such as Lab on a chip (LoC) devices (e.g., Beaton et al., 2017²¹), some of which are presently operational. Most wet chemistry systems are recalibrated *in situ* at regular intervals²². Typically, wet chemical analysers show high resolution, accuracy and precision with a moderate response time. However, they are limited by reagent and power consumption, cost, size, and weight.

The UV optical sensors are chemical-free because they are based on the UV absorption characteristics of seawater constituents. Currently nitrate is the only macronutrient that can be quantified using optical measurement principles. A broad spectral range is required to accurately resolve absorption spectra in complex media such as seawater as the detection of nitrate is based on deconvolution of absorbance spectra that include halogenates such as

²¹ Beaton, A.D., Wadham, J.L., Hawkins, J., Bagshaw, E.A., Lamarche-Gagnon, G., Mowlem, M.C., Tranter, M., 2017. High-Resolution *in situ* Measurement of Nitrate in Runoff from the Greenland Ice Sheet. *Environ. Sci. Technol.* *acs.est.7b03121*. <https://doi.org/10.1021/acs.est.7b03121>

²² Laes-Huon, A., Cathalot, C., Legrand, J., Tanguy, V., Sarradin, P.-M., 2016. Long-Term *in situ* survey of reactive iron concentrations at the Emso-Azores observatory. *IEEE J. Ocean. Eng.* *41*. <https://doi.org/10.1109/JOE.2016.2552779>

bromide^{23,24}. UV sensors are characterised by a wide concentration range, rapid response times, small size and low power consumption, enabling their deployment across both fixed and profiling observing platforms. However, their sensitivity and accuracy are poorer than those of wet chemical analysers due to a range of optical interferences (dissolved and particulate organic matter). Temperature and salinity compensation, and turbidity correction are required to enhance the analytical performances of the UV optical sensors. Signal drift due to biofouling on the optical measuring window has been observed especially in coastal waters over long deployments¹⁸.

Electrochemical sensors propose promising reagentless sensors that could facilitate miniaturisation and decrease energy requirements. Electrochemical methods have been developed to detect silicate²⁵ and phosphate²⁶ in seawater. As silicate and phosphate are non-electroactive compounds, a chemical reaction with molybdates under acidic pH is required to transform these nutrients into silico- and phospho-molybdic complexes. A simple oxidation of a molybdenum electrode is used to form in situ the reagents needed. These complexes are then detected on gold working electrode using cyclic or square wave voltammetry. The method has the benefit of being robust and simple because it is based on straightforward sample fluidics with no liquid reagent (Table 1). However, although the electrochemical reaction is performed in a few seconds, the total measurement time is about 30 min due to a rather slow pumping technology²⁷.

²³ Frank, C., Meier, D., Voß, D., Zielinski, O., 2014. Computation of nitrate concentrations in coastal waters using an in situ ultraviolet spectrophotometer: Behavior of different computation methods in a case study a steep salinity gradient in the southern North Sea. *Methods Oceanogr.* 9, 34–43. <https://doi.org/10.1016/j.mio.2014.09.002>

²⁴ Johnson, K.S., Coletti, L.J., 2002. In situ ultraviolet spectrophotometry for high resolution and long-term monitoring of nitrate, bromide and bisulfide in the ocean. *Deep. Res. Part I Oceanogr. Res. Pap.* 49, 1291–1305. [https://doi.org/10.1016/S0967-0637\(02\)00020-1](https://doi.org/10.1016/S0967-0637(02)00020-1)

²⁵ Barus, C., Romanytsia, I., Striebig, N., Garçon, V., 2016. Toward an in situ phosphate sensor in seawater using Square Wave Voltammetry. *Talanta* 160, 417–424. <https://doi.org/10.1016/j.talanta.2016.07.057>

²⁶ Jonca, J., Comtat, M., Garçon, V., 2013. In situ Phosphate Monitoring in seawater: Today and Tomorrow. *Real-Time Water Qual. Monit.* 4, 25–44. https://doi.org/10.1007/978-3-642-37006-9_2

²⁷ Barus, C., Legrand, D.C., Striebig, N., Jugeau, B., David, A., Valladares, M., Parra, P.M., Ramos, M.E., Dewitte, B., Garçon, V., 2018. First deployment and validation of in situ silicate electrochemical sensor in seawater. *Front. Mar. Sci.* 4, 1–11.

Table 1. Advantages and disadvantages of the analytical techniques used for the in situ determination of nutrients in seawater (Table 2 from Daniel et al., 2020²⁰).

TABLE 2 | Advantages and disadvantages of the analytical technologies used for the in situ determination of nutrients in seawater.

Advantages	Disadvantages	Optimal conditions of deployment	Tested deployment platforms	Claimed widest measurement range (LOD* – max. value) $\mu\text{mol/l}$	References
Wet chemical analyzers (spectrophotometry and fluorimetry)					
Limit of detection Low trueness Low precision: 1 – 4% Large concentration range for each nutrient In situ calibration Moderate response time (few min.) Not significantly affected by biofouling	High power requirements: 1, 5 – 28 W Relatively bulky: 500 x 200 mm, 5 – 8 kg High maintenance costs Longevity limited by reagent use and stability (1 – 5 months) Hazardous waste chemical storage	Coastal and open ocean, relatively short time periods (days to months) Temperate	FerryBox Buoy Benthic chambers Gliders Fixed platforms Mooredings	NO_3^- : 0.02–100 NO_2^- : 0.02 – 50 PO_4^{3-} : 0.04 – 50 NH_4^+ : 0.014–50 Si(OH)_4 : 0.05–250	- APNA, ChemFIN (Subchem systems, Egli et al., 2009) - WIZ (SYSTEA, Moschetti et al., 2009) - Micromac C (SYSTEA) - Hydrocycle PO4 (Seabird scientific) - NAS3X (Mills et al., 2005) - Digiscan (Plant et al., 2009) - ANAIS (Thouvenot et al., 2003) - Alchemist (Le Bris et al., 2000) - CHEMINI (Vuillemin et al., 2009a) - LoC (Beaton, 2012; Nightingale et al., 2015; Beaton et al., 2017; Clinton-Bailey et al., 2017; Grand et al., 2017; Vincent et al., 2018) - NuLAB (GreenEyes)
UV optical sensors					
Good trueness Large nitrate concentration range Reagent free Fast response: few seconds – 2 min Low power requirement: 4.2 – 8 W Moderate weight: 1.8 – 3.4 kg	Nitrate only Biofouling Subject to optical interferences Nitrate only Moderate limit of detection Moderate trueness	Coastal waters and open ocean, long time period (months to year), polar temperate and tropical	Buoy Profiling floats Gliders Mooredings	NO_3^- : 0.5–3200	- ISUS/SUNA (Seabird scientific; Johnson and Coletti, 2002; Johnson et al., 2006; D'Ortenzio et al., 2012, 2014; Frank et al., 2014) - ProPS/OPUS (TriOS; Zielinski et al., 2011; Meyer et al., 2018) - Spectrolyser (Scan Measuring Systems, Etheridge et al., 2014) - SUV-6 (Finch et al., 1998)
Electrochemical sensors					
Moderate silicate concentration range Reagent free Moderate weight: 2.2 kg Not significantly affected by biofouling	Silicate only Moderate limit of detection Moderate trueness Moderate precision: 2% Subject to large variation of salinity Long measurement cycle (30 – 60 min)	Coastal waters and open ocean, relatively short time period (days to months), polar temperate and tropical	Buoys Profiling floats	Si(OH)_4 : 1–140	- ANESIS (Lacombe et al., 2008; Jorica et al., 2013; Barus et al., 2016, 2018)
Benchmark techniques in laboratories					
All nutrients High trueness and precision Not affected by biofouling Moderate response time	Only discrete samples Potential contamination during the sampling Substantial and consistent maintenance Not optimized for long-term unattended operation	/	/	NH_4^+ : 0.002 – 25 NO_3^- : 0.01 – 500 NO_2^- : 0.002 – 2 PO_4^{3-} : 0.003 – 6 Si(OH)_4 : 0.03 – 200 <i>The high value corresponds to the value commonly encountered in estuaries, the value that can be analyzed may be higher</i>	- AA3 and QuAAro SEAL analytical - SkalarVR - Lachat QuikChem

*The authors of the references cited did not necessarily use the same way to calculate the Limit Of Detection. P, prototype; C, commercially available; S, end of sale.

Each sensor type will be suitable for a specific deployment purpose, application, platforms or monitoring strategy (Figure 1). The choice of an in situ nutrient device must be made ensuring that its analytical performance meets the monitoring objectives and considering the specific environmental factors of the study area. The expected analytical performance, the deployment platform and the characteristics of the water to be measured must be identified and taken into account when making the sensor choice. Weight, size, buoyancy, power requirements and communication bandwidth limitations on deployment platforms are also important considerations for data collection and transmission. Furthermore, it must be noted that the optimal benefit-cost ratio forms an important consideration and may be a major limiting factor, especially for expendable platforms such as drifters. Only dissolved inorganic nutrients can currently be measured by in situ sensors, dedicated instrumentation for the analysis of dissolved organic and particulate nutrients have not yet been developed. In addition to analytical performance, in situ devices have further requirements relative to laboratory techniques including physical robustness, resistance to biofouling, high pressure

and temperature variations, and stable long-term operation with low energy and, where relevant, low reagent consumption²⁸.

3.2. General considerations for near real-time data quality control of biogeochemical data

Data collected in near real-time is expected to be somewhat limited and incomplete. Due to the diverse sources, the nature of the data—e.g., the frequency in time, the spatial pattern, and the depth—varies greatly. However, the observations should provide sufficient data quality information on horizontal and vertical dimensions. The specific challenge with near real-time QC is evaluating the most current data point and is characterised by:

- Near real-time data is acquired typically from seconds to hours and can quickly be used for various purposes (e.g., model ingestion). It is often the case that operational modelling communities require data within 24 hours, require automated procedures, and know that the data has not been subjected to climate-grade QC. However, a rough QC is required to ensure that data assimilations are not harmed.
- Near real-time data can be a helpful source for management decisions and policymakers.
- In addition, near real-time data can be used to ensure that high-quality multiplatform observations are gathered and failures detected from on-board sensors.

The first step in quality control is the close monitoring of the near real-time observations from scientists at least every couple of days. Based on the nature of the near real-time QC, several levels can be distinguished:

- a) Checks for quick response are performed automatically.
- b) Automatic update once more information becomes available to better support an evaluation, like more vertical profiles available, deeper profiles to stable waters, comparison with other platforms available in the study area, changes on the instrument configurations, etc.
- c) Manual assessment is highly recommended. Experts need to keep a tight eye on the near real-time observations in the hopes of spotting something suspicious in the data.

Basic automatic QC tests have been developed for biogeochemical observations, as summarised in the deliverable Copernicus Marine in situ TAC BGC quality control group (2022)²⁹ and Real Time Quality Control of Biogeochemical Measurements (2015), Version 2.5 [MyOcean WP.15]³⁰. Table 2 summarises a series of QC tests that are automatically run to flag BGC variables.

²⁸ Mukhopadhyay, S.C., Mason, A., 2013. Smart Sensors for Real-Time Water Quality Monitoring 4, 295. <https://doi.org/10.1007/978-3-642-37006-9>

²⁹ Copernicus Marine in situ TAC BGC quality control group (2022). Real time quality control of biogeochemical measurements within Copernicus Marine in situ TAC. <https://doi.org/10.13155/75704>

³⁰ Jaccard, P.; Norli, M.; Ledang, A.B.; Hjermann, D.O.; Reggiani, E.R.; Sørensen, K.; Wehde, H.; Kaitala, S. and Folkestad, A. (2015) Real Time Quality Control of biogeochemical measurements. Version 2.5 [MyOcean WP.15]. Norway, NIVA, 40pp. DOI: <http://dx.doi.org/10.25607/OBP-213>

Table 2. Automatic BGC quality control tests developed by Copernicus Marine in situ TAC.

List of automatic BGC data test	Test description
Impossible date and location test	This metadata test checks whether the observation date, time, latitude and longitude from the profile data
Automated test for on-land position	Positions have been tested against both the ETOPO2 elevation data and the Global Self-consistent Hierarchical High-resolution Shorelines (GSHHS) dataset ³¹ .
Negative pressure test	This test checks whether the observation pressure or depth from the profile data is greater than or equal to 0, both for dbar and meter (depth/pressure is positive downwards)
Metadata and hydrological QC test [$\mu\text{mol/kg}$]	The test checks that the BGC parameter has been converted into valid temperature, salinity, and pressure.
Stuck Value test	This test checks whether the values of N consecutive measurements are identical.
Missing value test	This test checks for missing values, usually called Fill Values in netcdf file.
Global Range test	This test applies a gross filter on observed BGC values.
Regional Range test	This test is built to eliminate outliers in different geographical regions.
Spike and gradient test	Spike and gradient tests from BGC argo recommendations ² are combined here to detect single spikes along a vertical profile

3.3. Examples of near real-time multiplatform biogeochemical observations within JERICO-S3

The following subsections describe five examples of near real-time multiplatform biogeochemical observations that have been carried out within JERICO-S3 IRSs and PSSs. The examples include various combinations of biogeochemical EOVS dissolved oxygen, inorganic carbon, and dissolved organic matter, as well as other EOVS related to phytoplankton biomass, ocean colour, etc.

³¹ Wessel, P., and W. H. F. Smith (1996) A Global Self-consistent, Hierarchical, High-resolution Shoreline Database, J. Geophys. Res., 101, 8741-8743.

3.3.1. Example 1: Dissolved oxygen and chl a from buoy, glider, and research vessels in the Western Mediterranean Sea (SOCIB)

SOCIB has a multi-platform network of observing platforms that continuously monitor the Western Mediterranean Sea. The biogeochemical data at SOCIB originates mostly from gliders and moorings. As the variables and formats are diverse, such as the sampling frequency, the spatial distribution, and their depth, it is important to define different criteria for Real Time Quality Control (RTQC) and provide quality assurance procedures. In contrast to delayed mode QC, what distinguishes a QC approach for gliders and moorings as 'real time' or 'near real-time' is that both scientists and engineers may have a subset of data on land through satellite communication. The availability of data is influenced by the cost of satellite communication for both gliders and moorings. Furthermore, data availability for gliders is affected by surface time and operational risks.

The R/V SOCIB undertakes four seasonal Canales cruises every year, one of which is to gather lowered CTD profiles and sample bottle data to provide a baseline of high-quality delayed mode data for inter-calibration and harmonisation with the SOCIB's nearly continuous glider monitoring lines. During the Canales cruises, a CTD section is carried out across the Ibiza Channel (IC) and Mallorca Channels (MC), consisting of 20 stations in total. Measurements are made with a Sea-Bird SBE9+ instrument and the oceanographic Niskin bottle rosette for water samples at different depths. Samples are always taken for salinity, dissolved oxygen, and chlorophyll concentration, as these support the routinely mounted CTD instruments and those on the Glider vehicles.

The CTD cast will be coordinated as closely as feasible with an operational SOCIB glider in Ibiza Channel, with a minimum water depth of 500 meters. This cast is intended to further help the inter-calibration of the Glider data with the measurements acquired with the Sea-Bird SBE9+ instrument and the oceanographic Niskin bottle rosette for water samples from various depths.

A CTD cast from the R/V SOCIB is conducted as close as possible to the Bahia de Palma observing buoy taking safety concerns into consideration. The mooring is at one of the corner points that define the "Cabo Enderrocat Marine Reserve", specifically at 39° 29.933' N, 02° 42.128' E. Water samples from a depth of 0-3 metres are required in order to calibrate the biogeochemical data from the multi-disciplinary sensors on the buoy. However, this operation is not always possible or convenient, as a small boat is needed to get close to the buoy. This is a small deviation for the R/V SOCIB cruise programme, and therefore, if possible, it can be carried out both at the beginning and at the end of the Canales cruises. It does not replace the regular monthly maintenance/sampling programme at the buoy, it simply re-enforces the programme. The Monthly sampling was not always possible and some considerable gaps in sampling do exist.

Water samples for dissolved oxygen, total chl a, nutrients, phytoplankton taxonomic composition and salinity were taken at 1 or 1.5 m depth (depending on the year) with either a Niskin bottle or a water pump. For dissolved oxygen, discrete water samples for sensor comparison were analysed using the Winkler's method. For total chl a determination, the filtration procedure followed the same protocol established for the R/V SOCIB, and total chl

a determination (with no acidification) was carried out within 1-3 weeks after sampling and storage in a freezer using a fluorometer (Trilogy, 10/26 Turner Designs: <https://www.turnerdesigns.com/trilogy-laboratory-fluorometer>).

Instrument dissolved oxygen (DO) values were corrected to water bottle sample values where these existed using a gradient operator where possible, i.e.:

$$\text{Corrected(DO)} = A * \text{Observed(DO)}$$

However, it was clear that for some instrument deployments an offset may also be required, i.e., a first order polynomial function of the form:

$$\text{Corrected(DO)} = A * \text{Observed(DO)} + B.$$

Where water bottles did not exist over the duration of an instrument deployment, corrections could be made to ensure a jump free continuity with the proceeding or preceding deployment, or both where possible. In addition, the inverse relationship between the seasonal cycles in DO and temperature was used to constrain these delayed mode calibrations where possible; for example, a warmer summer period in any particular year should indicate a lower DO concentration than a cooler summer period in another year.

Fluorescence yield inferred chlorophyll values chl a were corrected to water bottle samples where these existed using a first order polynomial function of the form:

$$\text{Corrected Chl(a)} = A * \text{Observed Chl(a)} + B.$$

Where water bottles did not exist over the duration of an instrument deployment, corrections could be made to ensure a jump free continuity with the proceeding or preceding deployment, or both where possible. In addition, we were able to use the 'typical' level of noise around the very low or zero chl a values from deployments with a good number of water bottle samples in order to constrain the value of A, the gradient operator in the first order polynomial function above, this was particularly important where the instrument in one deployment clearly had a very high gain setting erroneously applied in its laboratory calibration. The offsets, B, in the first order polynomial function above were also constrained such that the zero background level was consistent across the entire period, 2013-2019.

3.3.2. Example 2: Coloured dissolved organic matter, chl a, carbonate chemistry from FerryBoxes and research vessels along the Norwegian coast (NIVA)

Coastal Norway can generally be characterised as having three modes of land-sea interaction. In the south/southeast region (Oslofjord, Skagerrak, Eastern North Sea), a strong freshwater signal comes from the Baltic outflow, riverine inputs from northern Europe/Germany, and local riverine inputs from large Norwegian rivers such as Glomma River. In the southwest region (Bergen, Trondheim, Bodø), year-round rainfall and some seasonal snowmelt results in moderate freshwater inputs that alternate with coastal marine water masses composed of North Atlantic waters. In the northern region (Lofoten, Tromsø,

and locations further north), a strong seasonal pattern is evident due to colder winter temperatures which secures freshwater as snow, followed by large and episodic riverine input of freshwater and riverine material during late spring and summer. While some regions are relatively “stable” during some times of the year, the episodic nature of snowmelt and riverine input (which is also partially dependent on watershed characteristics) can be challenging to observe and characterise in the coastal zone.

Traditional observations using CTD rosettes and/or sampling bottles on research vessels (both small and large) have been carried out in some areas for decades. This approach provides sampling opportunities throughout the water column at a single station that is repeatedly visited during the year and over several years. The observations that are made with a profiling CTD and the samples that are collected from sample bottles (e.g., Niskin bottles) following a well-documented and quality-controlled routine³² to provide data with a high level of confidence. However, there are several shortcomings with regards to research vessel collected data and improving observations and understanding of land-sea interactions that include: a) the station locations are fixed in order to provide time-series measurements, and the stations are not always well-situated to best capture riverine inputs into coastal waters, b) capturing episodic events can be difficult as it is only practical to visit stations a certain number of times per year (which is typically monthly, at best) and the sampling time is always planned in advance due to scheduling and logistics.

In order to improve observations of riverine inputs, multiplatform observations from research vessels, ships of opportunity (FerryBox) sensor-based observations and automated sampling, and river station sensors have been combined as a way to fill in spatial/temporal gaps in observations and to couple river/catchment processes with those in the coastal zone. Additionally, high quality station-based and samples collected by refrigerated autosamplers (analysed using well-documented protocols and techniques) are used to validate FerryBox collected data at cross-over points in both space and time. The observations include the following relevant variables: salinity, CDOM absorbance/fluorescence, dissolved organic carbon (DOC), and carbonate chemistry variables (total alkalinity [AT], total dissolved inorganic carbon [CT], pH, and pCO₂).

For example, during a two-year period in 2017 and 2018, observations representative of southern Norway, western Norway, and northern Norway (episodic and seasonal) riverine discharge, riverine total suspended matter, and riverine DOC were examined in relation to research vessel- and FerryBox-based coastal observations of salinity, CDOM, and DOC (see Figures 2 and 3; Frigstad *et al.*, 2020³³). The FerryBox observations provided a higher degree of temporal resolution as well as spatial resolution in waters adjacent to the station and riverine input locations. The research vessel station data provided validation data as well as variability with depth profile data that the FerryBox with a sampling depth of 4-5 m was unable to observe.

³² <https://www.miljodirektoratet.no/publikasjoner/2022/juni/okokyst-delfprogram-norskehavet-nordarsrapport-2021/>

³³ Frigstad, H., Ø. Kaste, A. Deininger, K. Kvalsund, G. Christensen, R.G.J. Bellerby, K. Sørensen, M. Norli, and A.L. King. 2020. Influence of riverine input on Norwegian coastal system. 2020. *Frontiers in Marine Science*, doi:10.3389/fmars.2020.00332

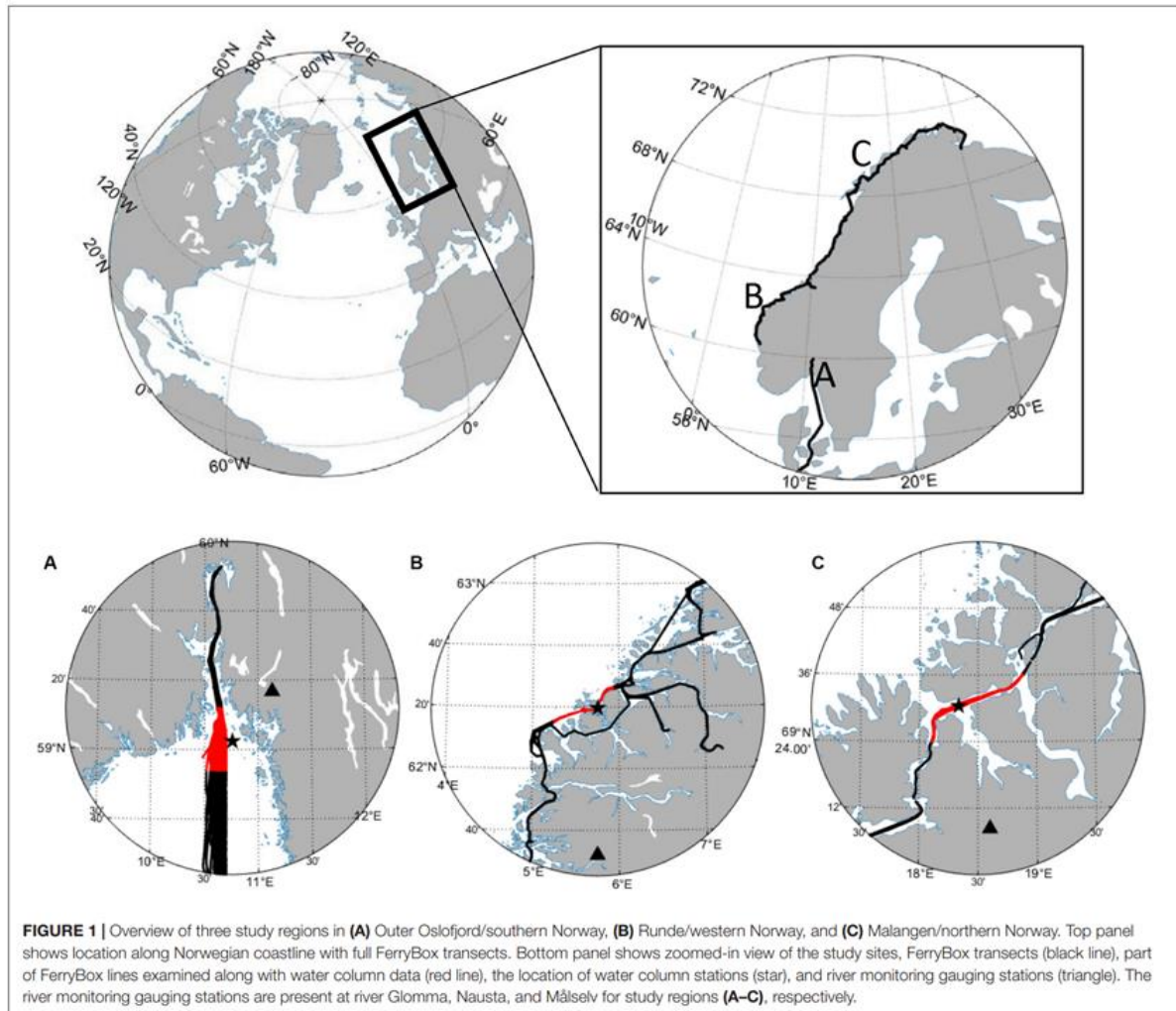


Figure 2. Overview of three study regions in A) Outer Oslofjord/southern Norway, B) Runde/western Norway, and C) Malangen/northern Norway. Top panel shows location along the Norwegian coastline with full FerryBox transects. Bottom panel shows zoomed-in view of the study sites. FerryBox transects (black line), part of the FerryBox lines examined along with water column data (red line), the location of water column stations (star), and river monitoring gauging stations (triangle). The river monitoring gauging stations are present at river Glomma, Nausta, and Målselv for study regions A-C, respectively. From Frigstad et al. (2020)³⁰.

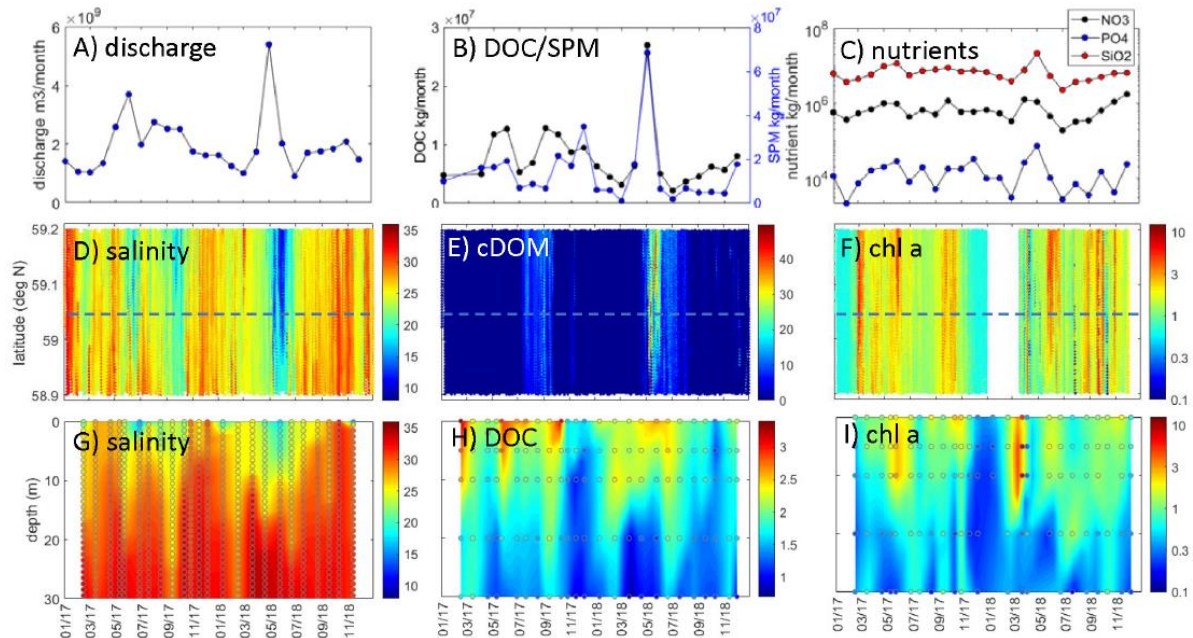


Figure 3. Outer Oslofjord/southern Norway observations. Glomma river: A) discharge ($\text{m}^3 \text{month}^{-1}$), B) DOC transport (kg month^{-1}) and SPM transport (kg month^{-1}), and C) nutrient transport (kg month^{-1} ; black: $\text{NO}_3\text{-N}$, blue: $\text{PO}_4\text{-P}$, red: $\text{SiO}_2\text{-Si}$). FerryBox observations within ~5-15 km east of coastal station: D) salinity, E) CDOM fluorescence (arbitrary), and F) chl a ($\mu\text{g L}^{-1}$; log scale). Water column station data (comparable latitude indicated by dashed blue line in panels D-F): G) salinity, H) DOC (mg L^{-1}), and I) chl a ($\mu\text{g L}^{-1}$; log scale). Data in D-I were interpolated with actual data points superimposed. From Frigstad et al. (2020)³⁰.

Further work related to multiplatform observations is also ongoing related to carbonate chemistry observations in coastal zones. For reasons similar to the example given above, research vessel observations are conventional due to the ability to collect samples throughout the water column and measuring the “gold standard” variables in oceanic carbonate chemistry measurements of AT and CT using lab-based instrumentation. However, the low temporal resolution (i.e., monthly or less frequent) and low spatial resolution (fixed stations) pose similar challenges in understanding carbonate system dynamics and ocean acidification state. For carbonate system dynamics, freshwater input from rivers can strongly influence CO_2 uptake or loss as changes in AT (typically reduction from freshwater inputs) can alter the buffering capacity of seawater and therefore surface water pCO_2 in relation to atmospheric pCO_2 . Additionally, the seasonality and duration of phytoplankton blooms can strongly affect carbonate system dynamics through drawdown of carbon dioxide (and total dissolved inorganic C) and eventual export to higher trophic levels or to deeper waters and/or the seafloor.

3.3.3. Example 3: Carbonate chemistry from a fixed platform and research cruises in the Adriatic Sea (CNR)

The Gulf of Trieste is a shallow bay (< 25 m) lying in the northernmost part of the Adriatic Sea, a sub-basin of the Mediterranean Sea. Meteorological conditions exhibit a pronounced seasonal cycle, which determines strong variations in seawater temperature, salinity and

water column stratification during the year³⁴. From October to March the water column is usually well mixed, with temperatures down to 9°C and only occasionally riverine plumes can reach the centre of the Gulf. During spring and summer, the temperature increases and the change of main circulation leads to the spreading of riverine plumes to the centre of the Gulf and a strong and variable thermohaline stratification develops with more than 10 °C of difference between the surface and the bottom³⁵. The PALOMA station hosts a meteorological station and is equipped with CTD, DO and pCO₂ sensors moored at 3 m average depth; it is located in the centre of the Gulf, in its deepest part, 8 nautical miles from the Isonzo river mouth and acquires near real-time data that that well represents the offshore variability (Fig. 4). The station is visited monthly to acquire a complete CTD profile and discrete samples for pH and AT analysis at the depth of the instruments and along the water column. pCO₂ is then calculated from pH and AT values along with T, S and nutrients (PO₄²⁻, SiO₃⁻) using the CO2SYS program (excel version 2.5; Orr *et al.*, 2018³⁶).

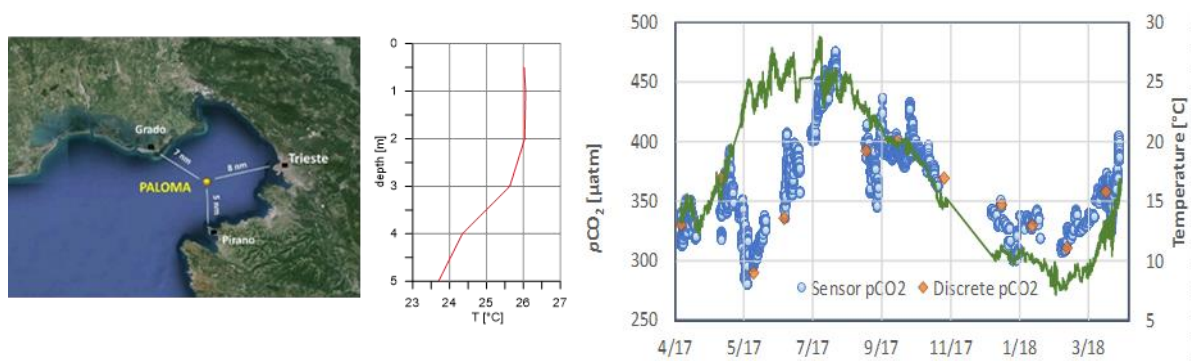


Figure 4. Map with the position of the station PALOMA (left); example of summer stratification (Aug. 2017, detail 0-5 m) (centre) and plot of temperature and pCO₂ measured at 3m avg. depth at the station (pCO₂ sensor), pCO₂ calculated from pH and AT discrete samples, from April 2017 to March 2018 (right).

pH and AT or pH and CT are the preferred couples of carbonate chemistry parameters to calculate pCO₂ as they minimise the resulting uncertainty (Orr *et al.*, 2018). This approach is commonly used to integrate ship-based discrete measurements with pCO₂ data measured with autonomous instruments (pCO₂ measured), but it is not straightforward, particularly in highly variable coastal areas, such as the Gulf of Trieste.

Even when instruments work perfectly and discrete measurements have high precision (accuracy of $\pm 0,003$ pH and ± 1 $\mu\text{mol/kg}$ AT), the error propagation within calculations, the error associated with carbonate system equilibrium constants, small differences in temperature, salinity or carbon chemistry can lead to high and variable uncertainties in

³⁴ Malačić, V., Petelin, B., 2001. Regional studies: gulf of Trieste. In: Cushman- Roisin, B., Gauci, M., Poulain, P.-M., Artegiani, A. (Eds.), Physical Oceanography of the Adriatic Sea: Past, Present and Future. Kluwer Academic Publishers, Dordrecht, pp. 167e181

³⁵ Cantoni, C., Luchetta, A., Celio, M., Cozzi, S., Raicich, F., Catalano, G., 2012. Carbonate system variability in the Gulf of Trieste (North Adriatic Sea). Estuar. Coast. Shelf Sci. 115, 51–62. <http://dx.doi.org/10.1016/j.ecss.2012.07.006>.

³⁶ Orr J. C., Epitalon J-M, Dickson A G., Gattuso J-P, 2018. Routine uncertainty propagation for the marine carbon dioxide system. Mar.Chem, 207, 84-107, <https://doi.org/10.1016/j.marchem.2018.10.006>.

calculated $p\text{CO}_2$ values ($p\text{CO}_2$ AT-pH) Fig 5. To identify the most challenging conditions and the main sources of uncertainty for measured $p\text{CO}_2$ and calculated $p\text{CO}_2$ AT-pH, we calculated the uncertainties on $p\text{CO}_2$ calculated from pH ($\pm 0,003$) and AT ($\pm 1 \mu\text{mol/kg}$) for the typical salinity and AT values of the Gulf of Trieste ($S=37$, $AT=2680 \mu\text{mol/kg}$) over the whole range of $p\text{CO}_2$ and temperatures measured over an annual cycle (Fig. 4).

The uncertainty is never lower than $5 \mu\text{atm}$ and linearly increases with $p\text{CO}_2$ values, with a steeper increase at lower temperatures. In the Gulf of Trieste higher $p\text{CO}_2$ are measured during summer where high temperatures help to minimise the increase of the uncertainty that spans from $5 \mu\text{atm}$ to $9 \mu\text{atm}$. Hence a good agreement between calculated and measured $p\text{CO}_2$ lies within this interval and an integration between the two kinds of observation is more accurate during winter, when low $p\text{CO}_2$ are observed, less accurate at higher $p\text{CO}_2$ values, particularly when coupled to low temperatures as can occur during wintry river floods.

The onset of the shallow thermohaline stratification leads to differences in temperature in a few metres and eventually the instruments are moored in between a steep temperature gradient, making difficult to accurately match CTD data with bottles when acquired in two different downcasts. The results reported in Fig. 5 indicate that a difference in temperature of $\pm 0.1^\circ\text{C}$, with no other changes in carbonate chemistry, leads to changes in $p\text{CO}_2$ lower than $\pm 2 \mu\text{atm}$. However, the effect of temperature on $p\text{CO}_2$ rapidly increases and a difference of $\pm 0.5^\circ\text{C}$ determine changes in $p\text{CO}_2$ spanning from $\pm 5 \mu\text{atm}$ at $p\text{CO}_2 = 250 \mu\text{atm}$ to $\pm 10 \mu\text{atm}$ at $p\text{CO}_2 = 450 \mu\text{atm}$. Repeating the calculations at 9°C and 26°C lead to similar results, underlining the importance of accurately handling surface temperature gradients and sampling depths in every season, when integrating data from different observing platforms, whether $p\text{CO}_2$ is calculated or directly measured.

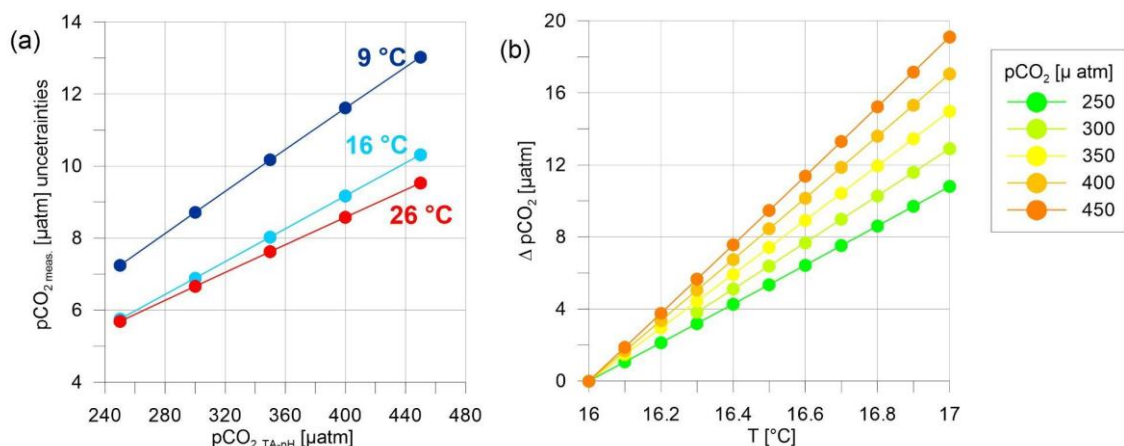


Figure 5. (a) uncertainty on $p\text{CO}_2$ calculated from pH and AT ($p\text{CO}_2$ pH-AT) as a function of $p\text{CO}_2$ at different temperatures. Input parameters: $S=37$, $AT=2680 \mu\text{mol/kg}$, pH uncertainty $\pm 0,003$, AT uncertainty $\pm 1 \mu\text{mol/kg}$; (b) difference between $p\text{CO}_2$ and $p\text{CO}_2$ at 16°C ($\Delta p\text{CO}_2$) as function of temperature, at different $p\text{CO}_2$ values calculated at $S=37$, $AT=2680 \mu\text{mol/kg}$.

3.3.4. Example 4: Carbonate chemistry observations from satellites, research vessels, fixed platform, and an atmospheric station (HCMR)

The Eastern Mediterranean Sea is an ultra-oligotrophic basin of the Mediterranean Sea, and it acts as a heat, salt, and oxygen reservoir. The area is characterised by multiple scale circulation patterns and intense mesoscale variability. In the region, vertical mixing leads to intermediate and deep-water formation. It is a hotspot of biodiversity; however, biodiversity long-term data sets are still limited. Like the other parts of the Eastern Mediterranean, the region is vulnerable to disturbances by invasion of alien species due to proximity to the Suez Canal. The northern part (North Aegean) is affected by material transport (nutrients, contaminants) from the Black Sea, large cities and rivers. In the southern part, atmospheric deposition is the main source of nutrients in the euphotic zone, other than the vertical mixing of water during winter. However, their exact contribution to the balance of nutrients and the resulting impact on productivity remains uncertain.

The Eastern part of the Mediterranean has greater sparseness of carbonate system data, leading to difficulties to understand its role as source or sink of CO₂. Most studies rely on discrete water samples acquired across different periods of time, covering limited regions of the Mediterranean. The scarcity of these research vessels (R/V) cruises results in large areas never being sampled due to long transit times and the high operating costs of R/V. On the other hand, time-series stations, until recently, were operating only at the Adriatic Sea, at high time-resolution and in the Levantine sub-basin, at low time-resolution³⁷.

Over the past few years, the POSEIDON system, the Eastern Mediterranean Ocean observatory dedicated to multiple in situ observations with a multiplatform-multivariable approach, is progressively integrating carbonate system sensors (pH & pCO₂) in its Cretan Sea component, the most platform-dense and BGC-ecosystem-oriented subsystem of POSEIDON³⁸. The added value of this multiplatform approach is explained below, using the example of carbonate variables, by the combination of observations from satellites, RV cruises, a marine fixed platform (buoy), an atmospheric station, as well as comparison with model results.

Since December 2020 a pH sensor and a pCO₂ sensor are deployed at subsurface in the Cretan Sea PSS on the POSEIDON Heraklion Coastal Buoy (HCB) providing pH and pCO₂ data every 3 to 6 hours (Fig. 6). In parallel, to check the sensors' operation and provide additional carbonate variables, during regular RV visits at HCB, water samples are taken for pH analysis as well as for CT and AT analysis. The data provided by the pH sensor, after processing, are in good agreement with data from samples. The comparison of seawater CO₂ from the sensor with estimates of CO₂ (calculated from pH and AT, and pH and CT of

³⁷ Hassoun A.E.R., E. Gemayel, E. Krasakopoulou, C. Goyet, M. Abboud-Abi Saab, P. Ziveri, F. Touratier, V. Guglielmi, C. Falco. Modeling of the total alkalinity and the total inorganic carbon in the Mediterranean Sea. *J. Water Resour. Ocean Sci.*, 4 (1) (2015), pp. 24-32

³⁸ Petihakis, G., Perivoliotis, L., Korres, G., Ballas, D., Frangoulis, C., Pagonis, P., Ntoumas, M., Pettas, M., Chalkiopoulos, A., Sotiropoulou, M., Bekiari, M., Kalampokis, A., Ravdas, M., Bourma, E., Christodoulaki, S., Zacharioudaki, A., Kassis, D., Potiris, E., Triantafyllou, G., Tsiaras, K., Krasakopoulou, E., Velanas, S. and Zisis, N. (2018). An integrated open-coastal biogeochemistry, ecosystem and biodiversity observatory of the eastern Mediterranean – the Cretan Sea component of the POSEIDON system. *Ocean Sci.*, 14(5), 1223–1245.

seawater samples) show a 15-20 μatm difference. In addition, the air CO_2 data provided from HCB are compared with a nearby atmospheric station (FINOKALIA) measuring air CO_2 . This comparison showed good correlation with a difference of approx. 5 ppm. In addition, using satellite data (SST, chl a), existing and new algorithms for CO_2 and AT estimation using satellite SSS, were tested. The analysis allowed the evaluation of existing carbonate algorithms from the literature proposed for the Eastern and entire Mediterranean Sea (five algorithms). The carbonate algorithm that uses SSS to calculate AT^{39} , which in combination with the pH in situ data allows to estimate the pCO_2 , showed the best agreement with the measured in situ pCO_2 data. Going one step further, the analysis led to the development of two new algorithms that use exclusively satellite data of a) SST and b) both SST and chl a data to calculate sea surface pCO_2 . The comparison of the output of these algorithms and the in situ collected data showed their importance as gap filling tool for missing parts of the in situ time series.

Finally, a coupled hydrodynamic-biogeochemical model POM-ERSEM-HALTAFALL was compared to the only model product (reanalysis) currently available for the Mediterranean (from CMEMS). In addition, a POM-ERSEM-HALTAFALL model, applied to the entire Mediterranean Sea at $1/10^\circ$ resolution, used data from multiple platforms: from the R/V METEOR mission to initialise the model, as well as from the NW Med PSS (DYFAMED, Villefranche-Point B), the Cretan Sea PSS (HCB) and the GLODAP database (i.e., cruises) to validate the model. The output of the two models is in good agreement for the pH and pCO_2 variables but deviates for the AT and CT variables (Fig. 7 and 8). The reasons for these discrepancies are under investigation.

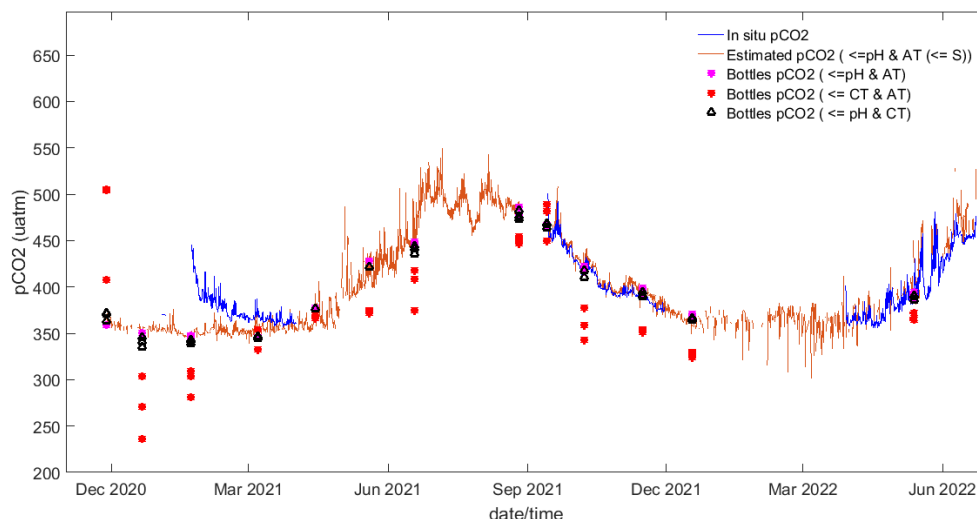


Figure 6. a) In situ pCO_2 (every 6h from sensor) (blue line), b) estimated pCO_2 from in situ pH from sensor & AT estimated from in situ S sensor (orange line), c) estimated pCO_2 from bottle pH & AT (magenta star), d) estimated pCO_2 from bottle AT & CT (red star), e) estimated pCO_2 from bottle pH & CT (black triangle).

³⁹ González-Dávila M., J. M Santana-Casiano, G. Petihakis, M. Ntoumas, M. Suárez de Tangil, E. Krasakopoulou, Seasonal pH variability in the Saronikos Gulf: A year-study using a new photometric pH sensor, *Journal of Marine Systems*, Volume 162, 2016, <https://doi.org/10.1016/j.jmarsys.2016.03.007>

In summary, the above example demonstrates how the multiplatform approach provided additional variables, gap filling tools, model improvement, optimum estimation method and optimum sampling strategy while improving the quality assessment of sensor operation. It is also important to mention that it created or enhanced interactions with ICOS, SOCAT and SOLAS.

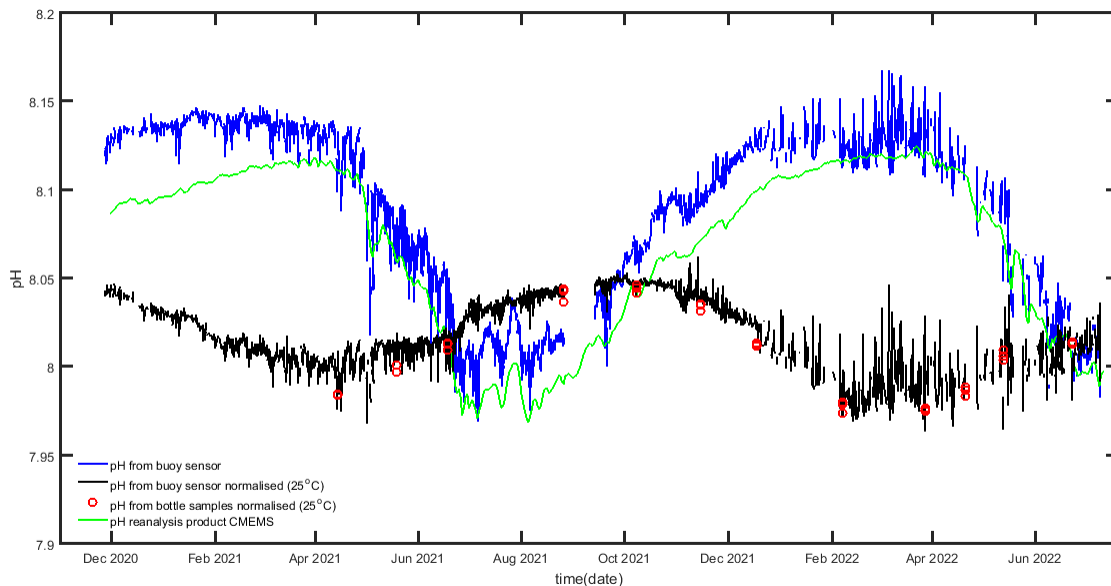


Figure 7. In situ pH (3h) at HCB buoy (blue), normalized to 25 °C (black), bottle reference data (red) and CMEMS reanalysis pH product.

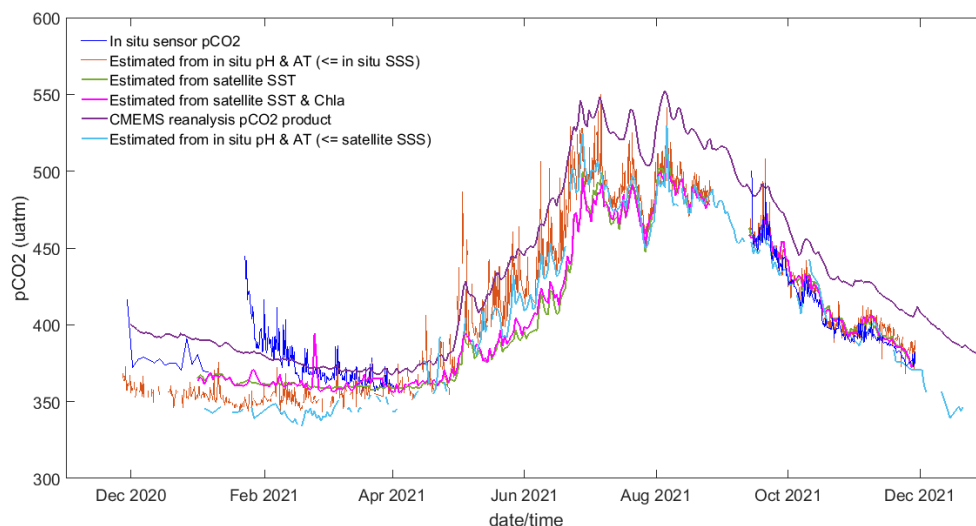


Figure 8. In situ sensor pCO₂ (blue) against estimated pCO₂ from in situ pH sensor & AT estimated from in situ S sensor (orange) or AT estimated from satellite SSS (cyan). AT estimation from salinity is made using the algorithm from González-Dávila et al. 2016³⁹. In addition, estimated pCO₂ with new algorithms using satellite SST-1var (green), SST & CHL-a-2var (magenta) and CMEMS reanalysis pCO₂ product (purple).

3.3.5. Example 5: Carbonate chemistry observations from fixed platforms and research vessels in the Northwest Mediterranean Sea (CNRS)

The Mediterranean Sea is a very dynamic regional sea. Because of its semi-enclosed nature and low inertia, due to the relatively short residence time of its water masses, it is highly reactive to external forcing variables, in particular to variations in water, energy and matter fluxes at the interfaces. The role of the Mediterranean Sea as a source or sink of atmospheric CO₂ in the global carbon cycle, especially in the context of warming Mediterranean Sea waters, is unclear. Several recent studies indicate a gradual shift from source to sink over the last decades. However, in situ measurements of the seawater carbonate system are still rare for the Mediterranean. In recent years, a few cruises have provided a clearer description of the carbonate system at the basin scale. For the north-western region, time series of carbonate chemistry exist in the Ligurian Sea at DYFAMED and ANTARES, in the Bay of Villefranche-sur-Mer at the Point B station, and in the Gulf of Trieste in the coastal water. However, these measurements are very spotty and do not allow us to understand the seasonal and interannual surface variability of the pCO₂-pH.

In recent years, technological advances have allowed the deployment of robust and quality pCO₂ and pH sensors at sea. Combined with pCO₂ measurements, these fixed-point measurements at the surface would allow a better estimation and understanding of the evolution of CO₂ fluxes at the air-sea interface. For this, the DYFAMED site already has high frequency pCO₂ measurements at the surface since 2013 and the installation of a new pH sensor (EUROSEA D3.6) will improve our CO₂ observations in the Ligurian Sea.

Since 2010, the fixed stations measuring continuously pCO₂-pH (surface buoys, deep mooring) and monthly discrete AT-CT-pH samples (coastal: Point B, SOLEMIO, MOLA; open sea: DYFAMED and ANTARES) have been extended by the annual MOOSE_GE cruise (ILICO-RI) which performs two CO₂ variables sections from Marseille to Menorca and Nice

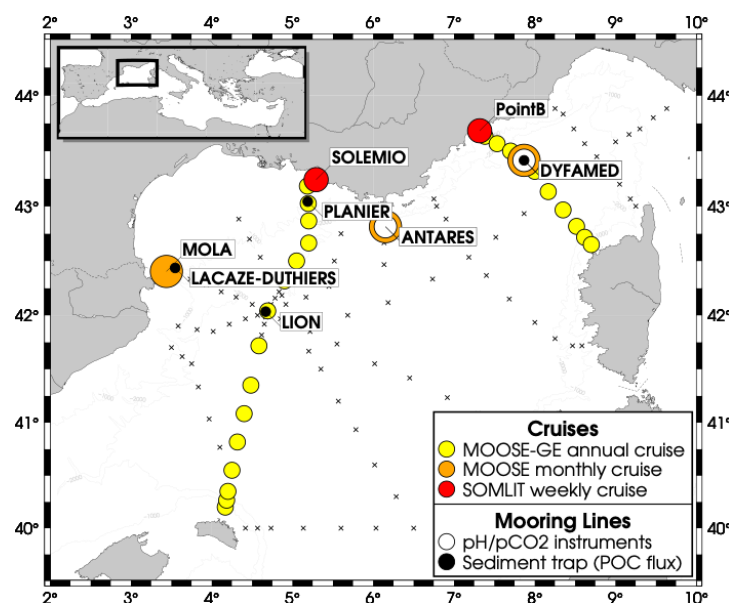


Figure 9. Location of CO₂ stations with discrete AT-CT-pH sampling and autonomous sensor measurements for pCO₂-pH.

to Calvi from surface to deep waters (Fig. 9). These datasets provide useful in situ measurements to constrain regional BGC model SYMPHONIE ECO3M-S able to produce CO₂ air-sea flux (Fig. 10) and vertical distribution of CT in this sub-basin (Ulses et al., submitted to Biogeosciences).

As an application example, we combined virtual and in situ observations to test the validity of predicted pCO₂ data and to fill gaps in pCO₂ time series measured by autonomous sensors (SBE37-ODO for TSO₂ and NKE CARIOCA for pCO₂) at the DYFAMED site in surface waters since 2013. Based on the corrections applied from monthly discrete samples (mainly O₂ with Winkler analysis), we observed a good match between in situ and predicted pCO₂ values and a good consistency in the predicted data to fill the pCO₂ time series (Fig. 11). This shows that a combination of in situ and virtual data with a regional CO₂ flux model is possible and will help us to better understand the CO₂ dynamics in the face of climate change in this region of the Mediterranean.

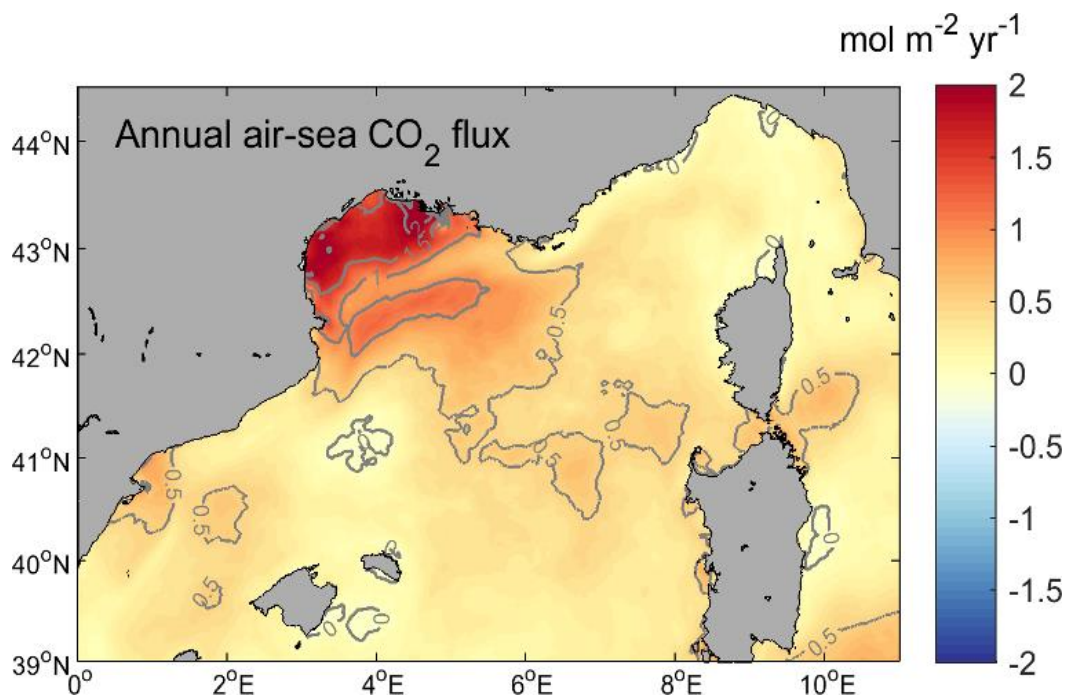


Figure 10. Schematic representation of neural network CANYON-MED providing nutrients and CO₂ variables from basic inputs variable (TSO₂) from Fourier et al. (2020)⁴⁰.

⁴⁰ Fourier, M., Coppola, L., Claustre, H., D'Ortenzio, F., Sauzède, R., and Gattuso, J.-P. (2020) A Regional Neural Network Approach to Estimate Water-Column Nutrient Concentrations and Carbonate System Variables in the Mediterranean Sea: CANYON-MED. *Front. Mar. Sci.* 7:620. doi: 10.3389/fmars.2020.00620

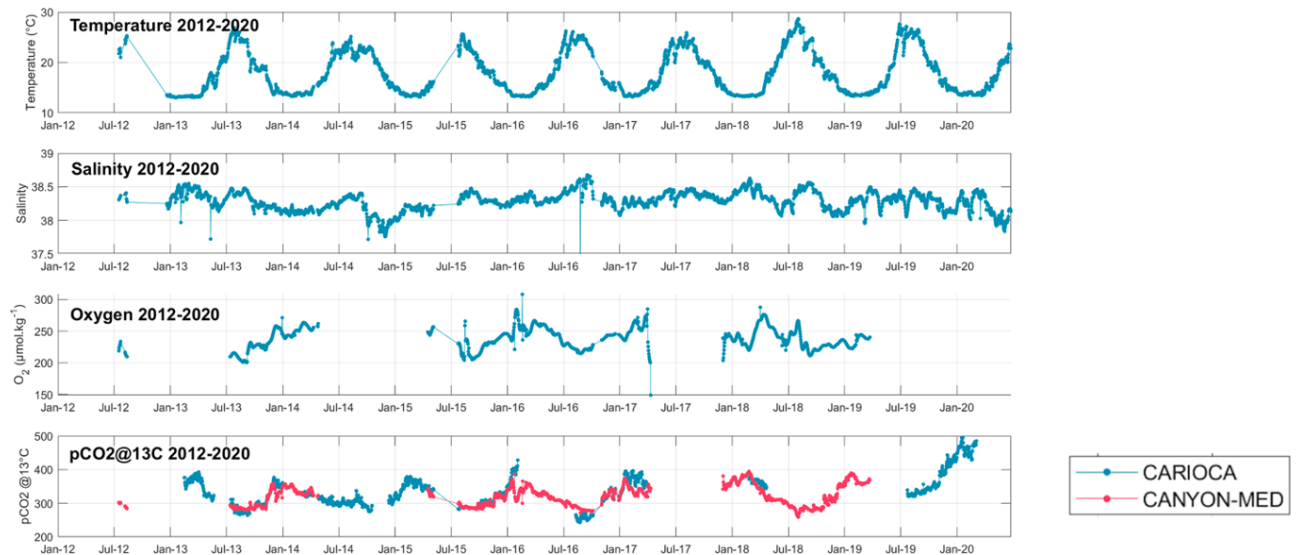


Figure 11. T-S-O₂-pCO₂ time series measured in surface waters at the DYFAMED site from 2013 to 2020.

3.4.Recommendations for near real-time biogeochemical observations

From the examples of multiplatform biogeochemical observations within JERICO-S3 in section 3.3, it is clear that increasing the quality of near real-time sensor data requires QC routines that ensure high quality data. As mentioned in the introduction, marine biogeochemical sensors are generally less mature and not as fully developed as sensors for physical EOVS like temperature and salinity. In some cases, what is measured by a sensor is a proxy or subset of the actual biogeochemical EOVS (see sections 3.1.2 on carbonate system chemistry and 3.1.3 on coloured dissolved organic matter). Biogeochemical sensor data requires a high degree of validation and calibration in order to assure the high-quality nature of the measurements. Sensors should follow calibration and validation techniques recommended in Section 3.1.

One type of QC for biogeochemical data involves QC routines or validation techniques that were exemplified above including comparison of biogeochemical sensor data to existing datasets and model outputs (regional or European level) (i.e., real-time or near real-time). The use of existing datasets and model outputs not only provides a range test that can be evaluated/implemented, but they also provide a wider/regional context for evaluating oceanographic consistency of biogeochemical variables.

A second type of QC in the examples above couples data to other observations made on other (autonomous) observing platforms and research vessel-based sampling followed by analysis of validation samples in the lab (i.e., delayed mode). In some cases, moving platforms (e.g., FerryBoxes or gliders) are in close proximity and/or pass by fixed platforms (e.g., buoys, moorings, terrestrial station) and make contemporaneous biogeochemical measurements of the same biogeochemical variable using similar sensor types. Remote sensing products can also be used for this type of multiplatform approach. In the case of

research vessel-based sampling, discrete water samples are collected and further processed/analysed using conventional oceanographic techniques that have been in use for, in some cases, decades. Discrete samples can also be collected on some platforms like FerryBoxes or large fixed platforms – this facilitates a high degree of spatiotemporal match-up to the sensor data. The discrete sample data are then used to validate and ground-truth biogeochemical sensor data in terms of drift. It should be noted that an example for nutrient observations was not provided, but similar QC principles can be implemented. Additionally, for carbonate system variables, algorithms such as CO2SYS or seacarb can be used to calculate other carbonate system variables (e.g., use pH and AT to calculate $p\text{CO}_2$) or perform so-called “overdeterminations” to compare inputs.

Recommendations for near real-time biogeochemical observations can be summarised as:

- Follow calibration techniques for the type of biogeochemical sensor that is used.
- Set QC routines based on existing datasets and/or model output for the observing region.
- Validate/compare data collected by other observing platforms measuring the same variable.
- Validate/compare data collected by a research vessel collecting discrete samples followed by lab analysis using traditional techniques.

The latter three recommendations are all, in fact, multiplatform approaches - various data sources collected by different platforms, synthesised and further processed, are then used to evaluate and increase quality of measurements. However, strictly speaking, if a network of observing platforms is well-coordinate and linked, it could be plausible that one observing platform could be calibrated and validated to a high degree with research vessel-collected samples (e.g., one fixed platform passed by various moving platforms), and the remaining observing platforms could then use the first observing platform as a reference station. Further work is required to establish and build such a system.

4. CONCLUSIONS

This Deliverable contains sections on the state-of-the-art of near real-time sensor observations of biogeochemical EOVs, examples of multiplatform observations including biogeochemical EOVs and other relevant EOVs, and recommendations for near real-time biogeochemical observations. Due to the higher degree of difficulty in making near real-time biogeochemical observations, it is recommended that: 1) sensors are calibrated according to best practices, 2) QC is performed with existing datasets and models, and 3) delayed-mode QC/validation is performed other measurements made at the observing platform (if possible) or by other complementary platforms including research vessel-based sampling followed by lab analysis. The last of the three recommendations, although a labour- and cost-intensive activity, is a reliable way of achieving high quality biogeochemical observations and could be considered as a requirement in future discussions. Marine biogeochemistry connects physical, biological, and chemical processes, and it is crucial to make high quality observations of biogeochemical EOVs in order to understand how coastal ecosystems function and vary over time.