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JGR Oceans

RESEARCH ARTICLE
10.1029/2022JC018615

Impact of Intermittent Convection in the Northwestern Mediterranean Sea on Oxygen Content, Nutrients, and the Carbonate System

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Key Points:

- In the absence of deep convection events, the O_2-depleted layer spreads vertically and intensifies more in the Ligurian than Gulf of Lion
- Nutrients increase in deep and to a lesser extent in intermediate waters with a decoupling between nitrate and phosphate trends
- Dissolved inorganic carbon increases in intermediate and deep waters with a concurrent pH decrease over the period of study, 2012–2020

Supporting Information:

Supporting Information may be found in the online version of this article.

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Citation:

Fourrier, M., Coppola, L., D'Ortenzio, F., Migon, C., & Gattuso, J.-P. (2022). Impact of intermittent convection in the northwestern Mediterranean Sea on oxygen content, nutrients, and the carbonate system. *Journal of Geophysical Research: Oceans*, *127*, e2022JC018615. https://doi.org/10.1029/2022JC018615

Received 8 MAR 2022
Accepted 23 AUG 2022

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Abstract Using Argo profiling floats, cruises and mooring data, we reconstructed the dissolved oxygen (O_2) dynamics in the Gulf of Lion and the Ligurian Sea, with a focus on the intermediate waters. By applying the CANYON-MED neural network-based method on the large network of O_2-equipped Argo floats we derived nutrients and carbonate system variables in the Gulf of Lion and the Ligurian Sea at different depths in the water column and derived trends over the 2012–2020 period. In these waters, the O_2 minimum is strongly affected by the intermittent convection process, and the two areas show dissimilar responses to the mixing events. In the absence of deep convection events, the O_2-depleted layer tends to spread vertically and intensify even more so in the Ligurian than in the Gulf of Lion. In both areas, over the 2012–2020 period, nutrients increase overall in deep layers, with a concomitant impact on nutrient molar ratios tending toward an increase in P-limitation. Acidification estimates derived in different layers of the water column show an overall increase in dissolved inorganic carbon and a concurrent pH decrease. These trends were strongly affected by convection events slowing down the overall acidification trend.

Plain Language Summary Using multiple observation platforms such as Argo profiling floats (autonomous, free-floating instruments equipped with sensors and profiling regularly in the first 2,000 m of the water column), cruises on oceanographic vessels, and moorings (fixed position stations), we reconstructed the dissolved oxygen (O_2) dynamics in the northwestern Mediterranean Sea. The intermediate waters are characterized by an O_2 minimum strongly affected by the intermittent convection process (due to winter forcings and density changes, mixing of water masses occurs over the water column). We also derived nutrients and carbonate system variables (related to acidification) from a neural network methodology developed for the Mediterranean Sea, CANYON-MED, applied to Argo floats equipped with O_2 sensors in different layers of the water column. Over the 2012–2020 period, the derived trends show an overall increase of nutrients in deep layers, with an impact on nutrient limitations. Acidification estimates show an overall acidification. These trends were strongly affected by convection events.

1. Introduction

The Mediterranean Sea is a semi-enclosed marginal sea characterized by a rapid overturning circulation (Millot & Taupier-Letage, 2005) where deep-water formation processes happen in both the western and eastern basins (Schroeder et al., 2012 and references therein, Pinardi et al., 2019). In the northwestern Mediterranean Sea, the intermediate water masses are characterized by a temperature and salinity maximum in subsurface corresponding to the Levantine Intermediate Waters (LIW) formed in the eastern basin in late February/early March (Lascaratos et al., 1993). This saline and relatively warm water mass spreads at intermediate depths (between 200 and 600 m) over the Mediterranean in a westward pathway, entering the Ligurian Sea and flowing within the Northern Current along the southern French coasts on its way to the Strait of Gibraltar. During its transit from the eastern basin, the consumption of organic matter sinking from the surface decreases the O_2 content in this water mass creating an O_2 minimum in the water column (160–170 µmol kg^{-1}, Coppola et al., 2018) and lowering pH_T and increasing dissolved inorganic carbon (C_T; Álvarez et al., 2014). In the northwestern Mediterranean Sea, which is well ventilated compared to the global ocean (Schneider et al., 2014), Dense Water Formation (DWF) mainly occurs in the Gulf of Lion (Herrmann et al., 2010; Somot et al., 2018), where winter

10.1029/2022JC018615

Writing – review & editing: Marine Fourrier, Laurent Coppola, Fabrizio D'Ortenzio, Christophe Migon, Jean-Pierre Gattuso

mixing of LIW with surface waters produces Western Mediterranean Deep Water (WMDW) during open sea deep convection (and sometimes during shelf water cascading). LIW is formed in the eastern basin and spreads to the western basin through the Strait of Sicily and the Corsica Channel. It is warmer and saltier than the WMDW and is a trigger for deep convection in winter (Testor et al., 2018). Recently the LIW has accumulated more heat and salt that has not been mixed due to the lack of deep convection (Margirier et al., 2020). Therefore, the water mass properties of the resulting WMDW vary according to the characteristics of the surface (MAW; Modified Atlantic Water) and intermediate waters (LIW). Due to intense convection events since the 2000s, the WMDW has experienced a significant increase in temperature and salinity with denser recent deep water under older deep water (Schroeder et al., 2016; Somot et al., 2018). In the Ligurian Sea, less intense DWF also occurs episodically (Somot et al., 2018; Sparnocchia et al., 1994). The Mediterranean Sea is considered an oligotrophic basin with low annual primary production (Moutin & Raimbault, 2002; Reale et al., 2020; Sournia, 1973) and an eastward increasing gradient of oligotrophy (Pujo-Pay et al., 2011). Winter vertical convection replenishes nutrients in the surface layers, and the efficiency of convection determines the availability of nutrients in photic waters (Mayot et al., 2017). The impact of these DWF events on physical variables has been thoroughly documented (Durrieu De Madron et al., 2017; Margirier, 2018; Testor et al., 2018). The consequences on O_2 and biogeochemistry were investigated during an intense observing effort in 2012–2013. Coppola et al. (2017) studied the ventilation of the deeper layers and estimated a newly ventilated dense water volume over that period of 1.5×10^{13} m^3, increasing the deep O_2 concentrations from 196 to 205 µmol kg^{-1}. Kessouri et al. (2017) analyzed the effect of DWF on biogeochemical budgets and primary production determining that the deep convection area acted as a sink of inorganic matter and a source of organic matter for the surrounding area together with a high variation of the N:P ratio in the surface layer during the transition between deep convection and loom periods. Finally, in the Ligurian Sea, a study by Coppola et al. (2018) analyzed the evolution of water mass characteristics and O_2 dynamics at the DYFAMED time-series station showing the effect of the intense convection of 2005–2006 on the ventilation of the water column and the risk of reaching hypoxia in intermediate water in 25 years if no major supply of O_2 and intense convection occurs regularly.

Changes in the deep-water properties of the western basin are primarily the result of surface properties modified by climate-related changes taking place at the air-sea interface which propagate downwards through deep-water formation (Touratier & Goyet, 2011). No study has characterized the temporal changes of O_2 in the two areas of the northwestern Mediterranean Sea subjected to DWF with spatial and temporal resolutions good enough to assess the O_2 response to winter mixing events. This is especially important as modeling studies project enhanced stratification and shallower Mixed Layer Depth (MLD) in the northwestern Mediterranean Sea (Pagès et al., 2020; Somot et al., 2006; Soto-Navarro et al., 2020). Such a scenario would reduce nutrient inputs from convection to nutrient-depleted surface waters, therefore impacting directly remineralization of organic matter and carbon export (Kessouri et al., 2018). Trends in the evolution of nutrients have been derived from ship-based studies but these remain limited in space through fixed stations such as DYFAMED (Pasqueron de Fommervault, Migon, D'Ortenzio, et al., 2015) or limited in time through yearly cruises (Kessouri et al., 2018). As for the evolution of the carbonate system in the northwestern Mediterranean Sea, most studies have focused on the surface layer and were either restrained spatially (DYFAMED, Coppola et al., 2020) or estimated changes relative to the preindustrial era (Hassoun et al., 2015; Touratier et al., 2016).

In the past decade, a large number of Argo floats equipped with O_2 sensors have been deployed in the Mediterranean Sea through multiple programs such as the French national initiative "Novel Argo ocean Observing System" (NAOS), a project to promote, consolidate, and develop the Argo network (e.g., D'Ortenzio et al., 2020; Le Traon et al., 2020) or MOOXY (2014–2019 GMMC project, CNRS) complementing the traditional observing systems (moorings, monthly and yearly cruises) and allowing better monitoring of O_2 dynamics in the area. Moreover, a neural network-based method CANYON-MED (Fourrier et al., 2020) has been developed for the Mediterranean Sea allowing estimates to be made for nitrate (NO_3^-), phosphate (PO_4^{3-}), silicate ($Si(OH)_4$), and carbonate system variables total alkalinity (A_T), total inorganic carbon (C_T), and pH on the total scale (pH_T) from temperature, salinity, O_2, geolocation and date of sampling. Therefore, by applying CANYON-MED on the large network of O_2-equipped Argo floats, biogeochemical variables can be derived and their temporal variations investigated, for example, in response to convection in a context of reduction of DWF events (Pagès et al., 2020; Somot et al., 2006; Soto-Navarro et al., 2020).

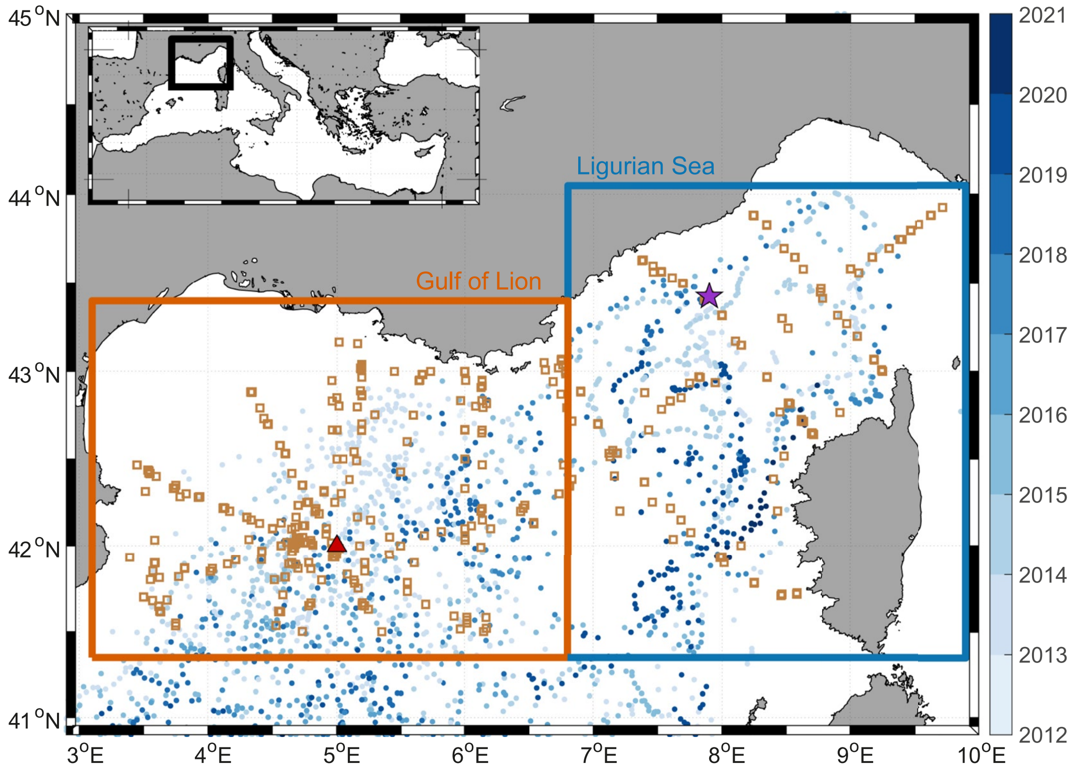

Figure 1. Position of Argo profiling floats profiles equipped with O_2 sensors according to the time of the profile (blue circles), stations from cruises (brown squares), and of the LION (red triangle) and DYFAMED (purple star) mooring sites in the Gulf of Lion (orange box) and Ligurian Sea (blue box), respectively.

This study aims to demonstrate how climate change can rapidly affect biogeochemical content throughout the water column (not only at the surface). Such trends have been studied mainly from fixed coastal sites or during research cruises with low vertical resolution. Furthermore, trends are often estimated only for surface waters. Here, the combination of high-frequency data (both in time and space) provided by BGC-Argo floats and fixed moorings with the outputs of the CANYON-MED neural networks provides new insight into basin-wide nutrient and carbonate trends for the intermediate and deep waters of the northwestern Mediterranean Sea which are poorly documented. With this aim, the O_2 time series reconstructed from Argo floats, moorings, and cruises in the Gulf of Lion and the Ligurian Sea, with a focus on the oxygen-depleted intermediate layer (LIW), are analyzed. Nutrients and carbonate system variables derived from Argo float data are described and the responses to DWF and trends at the surface, in intermediate waters, and at depth are discussed.

2. Materials and Methods

2.1. Study Area and Observational Data

2.1.1. DYFAMED and LION Sites

The DYFAMED site (Coppola et al., 2019) is located in the Ligurian Sea (43.41°N, 7.89°E, water depth of 2,350 m; Figure 1). It is surrounded by the permanent geostrophic Ligurian frontal jet flow caused by the Northern Current's cyclonic circulation, separating the sampling area from coastal inputs by a density gradient (Millot, 1999; Niewiadomska et al., 2008). Monthly cruises with full water column profiles have been performed at the DYFAMED site since 1991 and are included in the MOOSE network since 2010 (Coppola et al., 2019; Marty et al., 2002). This is the longest open-sea time series in the Mediterranean Sea in terms of O_2, nutrients, and carbonate system measurements. The LION site (Testor et al., 2020) is located in the Gulf of Lion (42.04°N, 4.68°E, water depth of 2,400 m, Figure 1) in the vicinity of the center of the DWF. At the two sites, moorings are equipped with CTD and oxygen sensors at intermediate depth (around 350 m) and 2,000 m. The oxygen data were corrected by applying a slope-offset correction to the Winkler reference data on samples collected monthly and yearly at DYFAMED and yearly at LION (Coppola et al., 2019).

Two regions are distinguished: the Gulf of Lion and the Ligurian Sea (Figure 1, orange and blue box respectively), with limits chosen at 6.9°E and 41.4°N taking into account regional dynamics (distance to the mixed patch in the Gulf of Lion and presence of episodic mixing in the Ligurian Sea with the influence of the Northern current and the Western Corsican current) and ensuring sufficient data in each area (1,560 profiles in the Gulf of Lion and 907 profiles in the Ligurian Sea).

2.1.2. Argo Floats

Data from 18 Argo (Argo, 2020) profiling floats equipped with O_2 sensors (Aanderaa optode) deployed in the Mediterranean Sea were used. Data span the period October 2012 (first deployments of Argo-O_2 floats in the area) to July 2020 (see Table S1 in Supporting Information S1 and Figure 1). The data set is composed of floats that were not specifically deployed or configured for this study but rather this study takes advantage of the sustained effort to deploy Argo-O_2 floats in the Mediterranean Sea. For almost all Argo floats (except 6902803 and 6902804), temperature and salinity were adjusted during "Delayed Mode" procedures. For the two Argo floats that did not go through Delayed Mode quality control procedures, a verification was done to ensure that the temperature and salinity values were consistent with the other floats in the data set and did not present abnormal values. Furthermore, to ensure consistency, only the O_2 data adjusted in "Delayed Mode" were used. For the adjustment, O_2 was checked by the Principal Investigator responsible for the float after adjustment as described by Bittig et al. (2019). Most floats were calibrated during "Delayed Mode" to a reference CTD cast or a climatological value. Only the more recent floats were able to do in-air measurements which they were corrected with, enabling a higher quality correction. Of the 18 floats in this study, four presented O_2 drift and were consequently corrected during the "Delayed Mode" procedures, and only two performed in air-measurements. Argo floats have been set up to profile every 1–5 days (higher sampling frequency when the floats were in the convective area during convective periods) to catch the O_2 variability with a 1,000 m parking depth. Some floats profiled upwards from 2,000 m to the surface while others profiled from 1,000 m to the surface.

2.1.3. MOOSE-GE Yearly Basin-Scale Cruises

Observations from the yearly MOOSE-GE cruises (Coppola & Diamond-Riquier, 2008) have also been used. The O_2 measurements were performed using a Seabird SBE43 sensor calibrated with Winkler measurements performed on board. Water samples were collected from CTD-rosette casts equipped with Niskin bottles. Seawater was sampled at different depths from the surface to just above the seafloor once per day. The calibration coefficients of the SBE43 sensor were adjusted for the whole cruise using the least squares method as described by Coppola et al. (2018).

Samples for dissolved inorganic nutrients were collected from Niskin bottles in 20 mL polyethylene bottles. They were analyzed by a standard colorimetric method on a segmented flow analyzer (Autoanalyzer II Seal Bran & Luebbe®) following Aminot and Kérouel (2007).

Samples for C_T and A_T were collected into acid-washed 500 cm^3 borosilicate glass bottles and poisoned with 100 mm^3 of $HgCl_2$, following the recommendation of Dickson et al. (2007). Samples were stored in the dark at 4°C pending analysis. Measurements of C_T and A_T were performed simultaneously by potentiometric acid titration using a closed-cell following the methods described by Edmond (1970) and Dickson and Goyet (1994). Analyses were performed at the National facility for the analysis of carbonate system parameters (SNAPO-CO2, LOCEAN, Sorbonne Université—CNRS, France).

2.2. Derived Variables

Seawater pH on the total scale at *in situ* pressure and temperature was derived from A_T and C_T data for the MOOSE-GE cruises. Calculations were performed using CO2SYS-MATLAB (Lewis et al., 1998; van Heuven et al., 2011) using the carbonic acid dissociation constants of Mehrbach et al. (1973) as refit by Dickson and Millero (1987), the dissociation constant for bisulfate of Dickson (1990) and Uppström (1974) for the ratio of total boron to salinity.

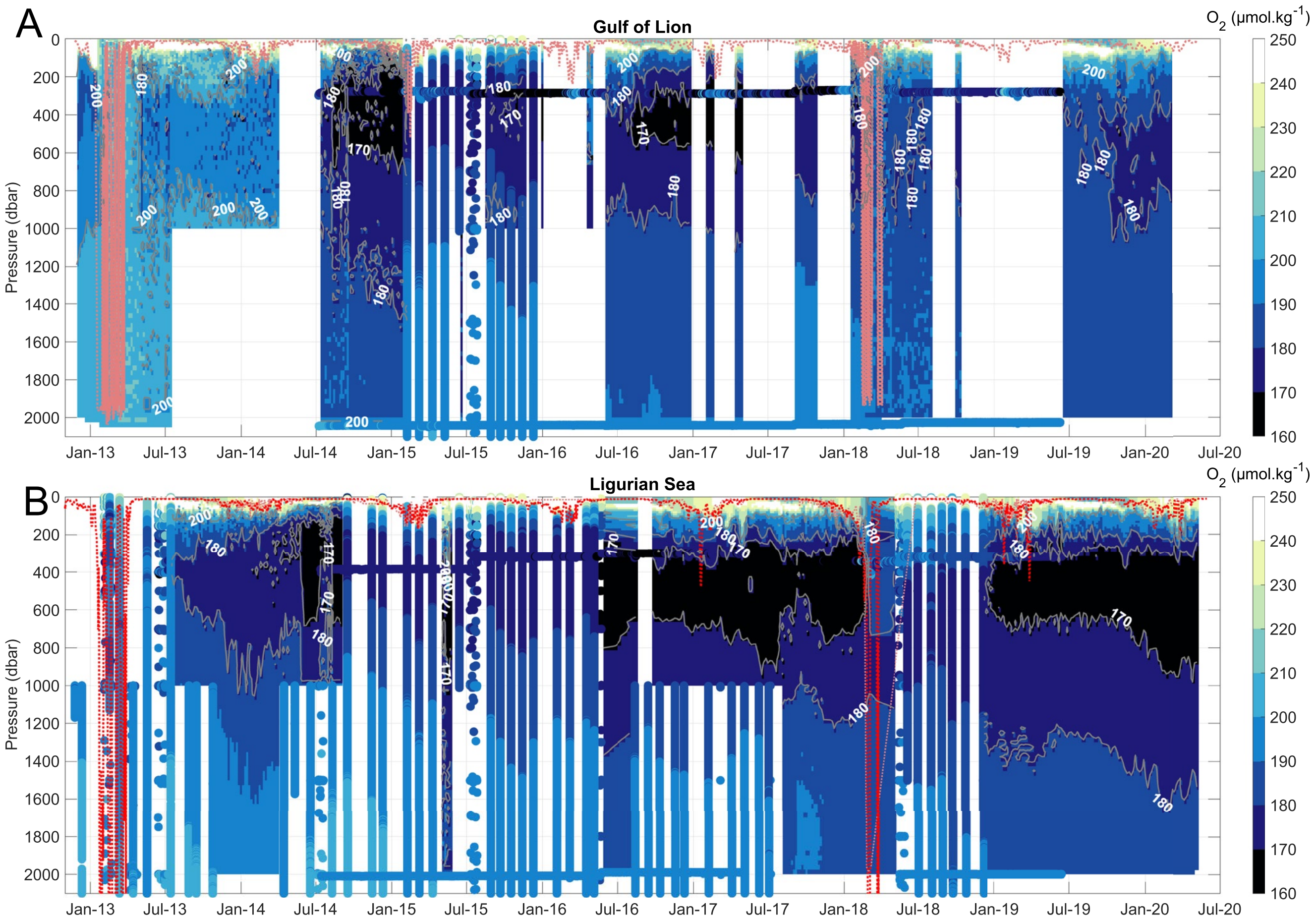

Figure 2. Time series of O_2 from profiling floats, moorings, and cruises in the (a) Gulf of Lion and (b) Ligurian Sea, and Mixed Layer Depth (MLD; dark redline). Individual points are bottle measurements and filled contours are Argo float measurements. For the Ligurian Sea, the median modeled MLD (bright red line) is presented when the MLD could not be derived from Argo floats.

The MLD was estimated for each float profile based on potential density profiles calculated from pressure, temperature, and salinity data. The MLD was derived using a 0.03 kg m^{-3} threshold density criterion with a reference depth of 10 m (D'Ortenzio et al., 2005). The maximum Argo-derived MLD is restricted to 2,000 m, that is, the maximum depth reached by the Argo floats.

In the Ligurian Sea over the period of study, few Argo floats were located close to the DYFAMED mooring. As the position of these Argo floats did not allow us to resolve the temporal variation of MLD at the position of the fixed time series, the MLDs calculated from a 3D-numerical simulation were used. These estimates were obtained from a simulation of the Mediterranean basin using the SYMPHONIE model (Marsaleix et al., 2008). This model has already been used to simulate convection in the northwestern Mediterranean (Estournel et al., 2016; Herrmann et al., 2008) and its impact on biogeochemistry (Kessouri et al., 2018) and oxygen budget (Ulses et al., 2021) for which the MLD is a key parameter. Furthermore, the MLD calculated by this model at DYFAMED was also used by Heimbürger et al. (2013) and Pasqueron de Fommervault, Migon, Dufour, et al. (2015). The numerical domain of the model has a mesh size ranging from 0.8 km in the north to 1.4 km in the south of the Mediterranean Sea (Ulses et al., 2021). In the present study, the daily median MLD using the 0.03 kg m^{-3} criterion over a 20 km area around the DYFAMED location was extracted from the simulation (Supplementary data, Figure S4 in Supporting Information S1) and is used for the Ligurian Sea in Figures 2 and 3.

In the western Mediterranean Sea, the O_2 Minimum Layer (OML) often coincides with the mean LIW depth (300–450 m; Tanhua et al., 2013). In this layer, O_2 consumption is higher than O_2 replenishment through diffusive and advective processes (Coppola et al., 2018; Packard et al., 1988; Tanhua et al., 2013). In this study, the depth of the LIW was determined as either the salinity or temperature maxima deeper than the 29 kg m^{-3} isopycnal.

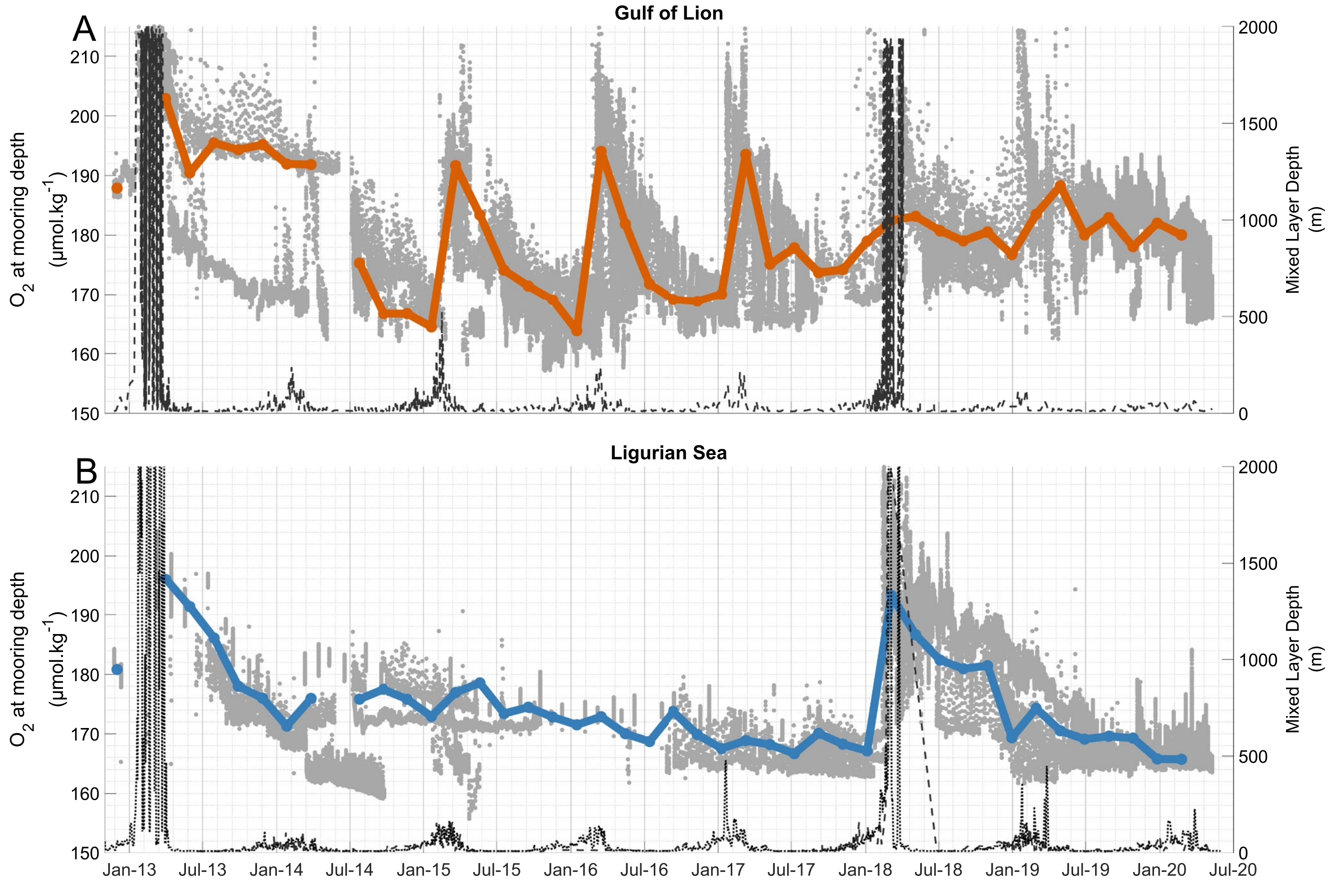

Figure 3. Time series of median O_2 at the depth of the mooring's O_2 sensor in the Gulf of Lion (a, orange) and the Ligurian Sea (b, blue) from all platforms. The colored line represents the median signal. The Mixed Layer Depth (MLD in meters, black line) was computed with a 0.03 density threshold (D'Ortenzio et al., 2005). For the Ligurian Sea, the median modeled MLD is presented when the MLD could not be derived from Argo floats.

Margirier et al. (2020) proposed this method as a way to better track the LIW in the T/S space rather than restricting it to a fixed depth. In some winter profiles, the water column is completely homogenized due to mixing, therefore the depth of the LIW was determined in this homogeneous layer. Furthermore, the OML was defined as the layer spanning 75 m above and below this depth.

To study the impact of winter convection events on intermediate layers, Argo float data are compared with mooring data (DYFAMED for the Ligurian Sea profiles, and LION for the Gulf of Lion profiles) at the corresponding depth, and with bottle data less than 15 days apart and less than 20 km apart.

The CANYON-MED neural networks are ensembles of two-hidden layers artificial neural networks developed specifically for the Mediterranean Sea that retrieve nutrients and carbonate system variables from temperature, salinity, O_2, geolocation and date of sampling. They were trained on a data set of quality controlled "bottle" data from 1976 to 2018 and validated against a Mediterranean timeseries (see details in Fourrier et al. [2020]). CANYON-MED retrieved the variables with good accuracies for the global Mediterranean Sea (Root Mean Squared Error): 0.78 µmol kg^{-1} for NO_3^-, 0.043 µmol kg^{-1} for PO_4^{3-} and 0.71 µmol kg^{-1} for $Si(OH)_4$, 0.014 units for pH_T, 13 µmol kg^{-1} for A_T and 12 µmol kg^{-1} for C_T. By applying the CANYON-MED neural networks (Fourrier et al., 2020), NO_3^-, PO_4^{3-}, $Si(OH)_4$, A_T, C_T, and pH_T were derived from float data.

2.3. Statistical Analyses

Temporal trends over the period 2013–2020 were computed at different depths for the biogeochemical variables of interest from CANYON-MED predictions from Argo float data. After removing the seasonal component through a yearly moving average, we used a Student *t*-test to detect trend significance (p-value < 0.01) from these yearly values in each area.

3. Results

3.1. Variability of the O_2 Concentrations in the Northwestern Basin

Figure 2 shows the time series of O_2 in the Gulf of Lion (Figure 2a) and Ligurian Sea (Figure 2b) as reconstructed from Argo floats, mooring data, and monthly and yearly cruises. For each area, O_2 data was interpolated over a grid with a 5-day step and with an adapted vertical resolution (metric over the first 10 m, with a 10 m-step until 200 m, and a 25 m-step until the bottom). Mooring data, monthly and yearly cruises were filtered down to a 5-day sampling frequency and gridded on the same grid as the Argo data. The coupling of these high-frequency measuring platforms allows for a reconstruction of O_2 dynamics in the two areas. In the Gulf of Lion, MLD increases to around 2,000 m in the winter 2012–2013 and to 1,900 m at the beginning of 2018. In the Ligurian Sea, monthly cruises allow for a reconstruction of the O_2 time series with fewer gaps than for the Gulf of Lion (Figure 2b). However, fewer Argo floats are located in the area, and float-derived MLD data is sparse. Therefore, specifically for the Ligurian Sea, a modeled MLD (median of 20 km around DYFAMED) is also used in addition to the incomplete Argo-derived MLD. O_2 follows the classical vertical distribution with higher O_2 in surface waters in contact with the atmosphere (>225 μmol kg^{-1}), a minimum in intermediate layers (OML in the LIW), and a subsequent increase with depth. The O_2 minimum spreads in the Gulf of Lion between 300 and 600 m with concentrations lower than 170 μmol kg^{-1}. In the Ligurian Sea, the O_2 minimum in intermediate waters spans from 250 to more than 600 m with a mean concentration of around 165 μmol kg^{-1}. In both areas, the O_2 minimum is periodically interrupted in winter.

In the deep layers, the lack of data prevents getting a clear picture of the effects of the deepening of the mixed layer depth on O_2, with the exception of the winter of 2012–2013 when a deepening to more than 2,000 m was captured by Argo floats and increased the O_2 concentration at depth to about 205 μmol kg^{-1} (Figure 2a). O_2 slowly decreased from 203 μmol kg^{-1} to 193 μmol kg^{-1} between summer 2014 and summer 2019. In contrast to the 2012–2013 winter mixing, the event of winter 2018–2019 did not affect the O_2 concentration trend at the depth of the deep mooring. Furthermore, the 2013 convective event in the Gulf of Lion may have induced increases in O_2 at depth in the Ligurian Sea through dense water spreading (Coppola et al., 2017), and the 2018 increase in O_2 at depth may result from a combination of the Ligurian Sea deep convection and the spreading of water masses from the Gulf of Lion deep convection. However, the OML is ventilated through local convective events.

To better study the effect of deep-water formation on the O_2 minimum in the intermediate layers (OML) of the northwestern Mediterranean Sea, Argo, mooring, and cruise data were extracted at the depth of the mooring's O_2 sensor (around 350 m), for the Gulf of Lion (Figure 3a) and the Ligurian Sea (Figure 3b). In the Gulf of Lion at the depth of the mooring's O_2 sensor, O_2 ranges from 160 to 210 μmol kg^{-1}. All instrumental platforms show periodic increases of O_2 followed by subsequent decreases over time. There is a strong covariance of O_2 from Argo, mooring, and cruise data at the mooring depths (Figure S1 in Supporting Information S1). These platforms used together allow a better reconstruction of the O_2 dynamics. In the Ligurian Sea, Argo floats data are scarce. O_2 also ranges from 160 to 210 μmol kg^{-1} in this area. All platforms capture a strong O_2 increase in winter 2013 (around 30 μmol kg^{-1}) and at the beginning of 2018 (up to 40 μmol kg^{-1}).

Based on the consistency of the different platforms used in this study (detailed in Figure S1 of Supporting Information S1), a median O_2 signal using all available data was derived in both areas of study at the mooring depth and is presented in Figure 3, together with the MLD from Argo floats and modeled MLD for the Ligurian Sea (same as in Figure 2) in both areas. In the Gulf of Lion (Figure 3a), there is a yearly seasonal cycle with increases in winter (highest values around February) and decreases from April onwards until the following winter. In winter 2012–2013, O_2 increased in the intermediate layers up to 210 μmol kg^{-1}. The spatial variability remained high in summer 2013 as demonstrated by the spread around the median value (about 20 μmol kg^{-1} of difference). From January 2013 to January 2014, an Argo float left the mixed area explaining the decreasing signal from 190 to 170 μmol kg^{-1} by January 2014. Variations occur in the yearly seasonal cycle with an increase in the minimum values of around 10 μmol kg^{-1} between the end of 2014 and the end of 2019.

In the Ligurian Sea (Figure 3b), O_2 in the intermediate waters does not exhibit the same yearly seasonal cycle as the Gulf of Lion. In winter 2013, O_2 in the OML increased from 180 μmol kg^{-1} at the end of 2012 to a higher

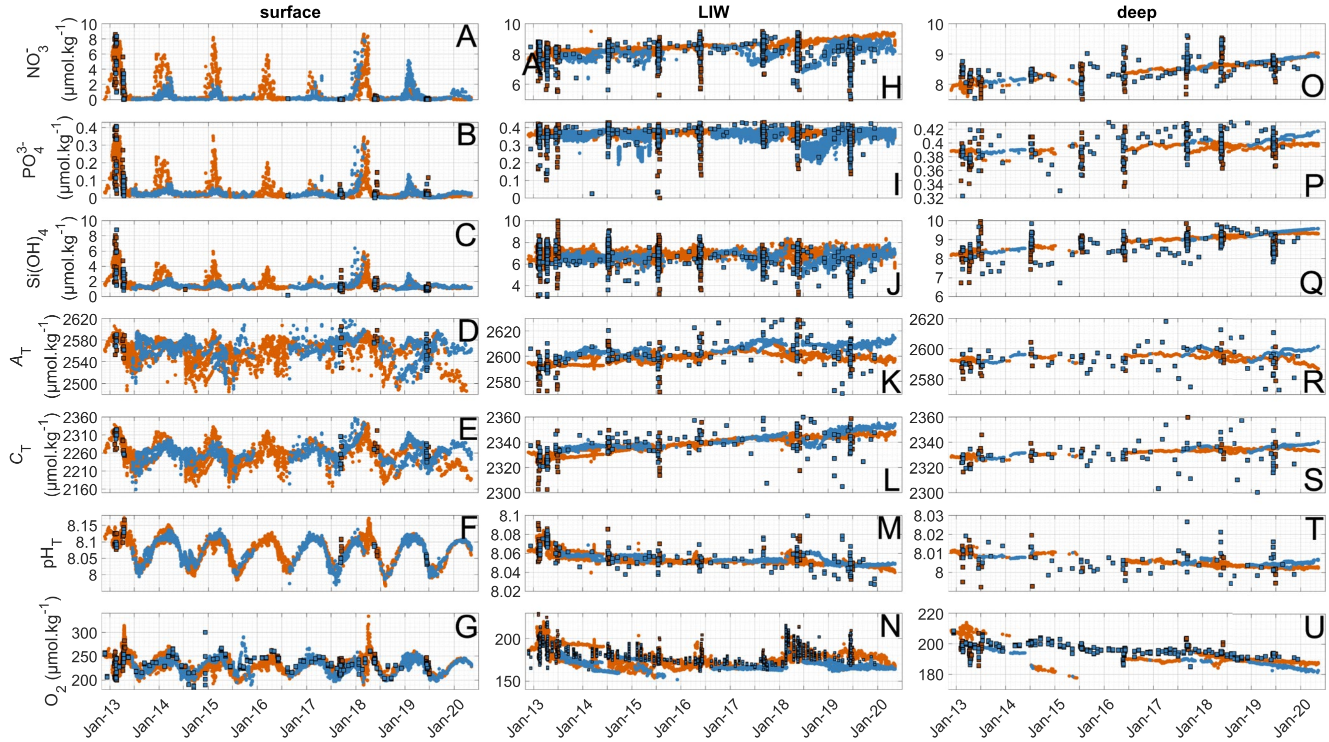

Figure 4. Biogeochemical evolution of the northwestern Mediterranean Sea. Panels (a–g) show the evolution in the surface waters (with high seasonal variability), panels (h–n) at the intermediate waters (in the OML), and panels (o–u) at 2,000 m, (a, h, and o) for nitrates, (b, i, and p) phosphates, (c, j, and q) silicates, (d, k, and r) total alkalinity, (e, l, and s) total carbon, (f, m, and t) pH_T and (g, n, and u) dissolved oxygen. The range changes between panels to better represent the values in the corresponding layer. CANYON-MED derived values from Argo float data are represented as dots (orange for the Gulf of Lion and blue for the Ligurian Sea). Bottle measurements are superimposed as colored squares according to their area. The bottle data come from a 15 day- 25 km- matchup with the CANYON-MED derived values from Argo floats.

amount (more than 200 µmol kg^{-1}) and returned to 170 µmol kg^{-1} almost a year later. Afterward O_2 steadily decreased between January 2014 and January 2018 by 0.5 µmol kg^{-1} year^{-1} in that area. At the beginning of 2018 O_2 increased up to 210 µmol kg^{-1} in the OML with a slow decrease afterward. One year later, in June 2019, O_2 remained higher than the year before leveling with values around 170 µmol kg^{-1}. From October 2019 onwards, O_2 remained stable.

3.2. Carbonate and Nutrient Variability

CANYON-MED-derived nutrients and carbonate system variables at the surface, in intermediate layers (in the OML), and at depth (around 2000 m) in the Gulf of Lion and the Ligurian Sea agree well with the data collected during the monthly and yearly cruises (Figure 4; Figure S2 in Supporting Information S1).

At the surface, all variables display clear seasonal cycles with large amplitudes, also present in the bottle reference data (squares on Figure 4) and no clear trend emerges at that depth. Nutrients exhibit a maximum at the end of winter and a minimum in summer, with a seasonal range two times larger in the Gulf of Lion than in the Ligurian Sea. A_T, C_T, and pH_T also vary seasonally with maxima in winter and minimal values in summer. There is no clear difference between the two areas in terms of seasonal range. In both areas, lacking data in specific seasons or years hinder the analysis of the seasonal cycles.

In the OML and at depth, nutrients, C_T increased throughout the 2013–2020 period as pH_T decreased (Figure 4, Table 1, Figure S3 in Supporting Information S1). However, the rate of change differs between regions (Gulf of Lion vs. Ligurian Sea) and depths (OML vs. 2,000 m). In the Gulf of Lion in the LIW, only NO_3^-exhibit an increase over the 2013–2020 period. During the winters 2012–2013 and 2017–2018, nutrients present a large range (up to 2 µmol kg^{-1} for NO_3^-). In the Ligurian Sea, no trend is significant in the OML. At about 2,000 m, the three macronutrients increase over the study period, and the impact of the 2012–2013 winter event and, to a lesser

Table 1
Estimates of Nutrients and Carbonate Variable Changes in the Northwestern Mediterranean Sea Calculated From the Yearly Averages in Figure S3 of Supporting Information S1

Variable	Area	Data type	Period	Surface trend	OML trend	Deep trend	Reference
NO_3^-(μmol kg^{-1})	GOL	CANYON-MED	2013–2020		0.158 ± 0.03	0.135 ± 0.05	This study
	LIG	CANYON-MED	2013–2020			0.129 ± 0.08	This study
	LIG	Shipborne	1991–2011			0.23%	Pasqueron de Fommervault, Migon, D'Ortenzio, et al. (2015)
PO_4^{3-}(μmol kg^{-1})	GOL	CANYON-MED	2013–2020			0.0016 ± 0.0016	This study
	LIG	CANYON-MED	2013–2020			0.0034 ± 0.002	This study
	LIG	Shipborne	1991–2011			−0.62%	Pasqueron de Fommervault, Migon, D'Ortenzio, et al. (2015)
$Si(OH)_4$ (μmolkg^{-1})	GOL	CANYON-MED	2013–2020			0.175 ± 0.078	This study
	LIG	CANYON-MED	2013–2020			0.187 ± 0.111	This study
	LIG	Shipborne	1991–2011			0.60%	Pasqueron de Fommervault, Migon, D'Ortenzio, et al. (2015)
A_T (μmol kg^{-1})	GOL	CANYON-MED	2013–2020				This study
	LIG	CANYON-MED	2013–2020				This study
	LIG	Shipborne	1998–2016	0.5 ± 0.21	0.80 ± 0.08	0.84 ± 0.132	Coppola et al. (2020)
C_T (μmol kg^{-1})	GOL	CANYON-MED	2013–2020		2.73 ± 0.60	1.20 ± 0.39	This study
	LIG	CANYON-MED	2013–2020		2.56 ± 1.31	1.60 ± 1.13	This study
	LIG	Shipborne	1998–2016	0.59 ± 0.34	1.18 ± 0.09	1.36 ± 0.161	Coppola et al. (2020)
	LIG	Mooring	1995–1997, 2013–2015	1.40 ± 0.15			Merlivat et al. (2018)
pH_T	GOL	CANYON-MED	2013–2020		−0.0022 ± 0.016	−0.0016 ± 0.0005	This study
	GOL	TrOCA method	Preindustrial—2011	−0.15 to −0.11	−0.15 to −0.11	−0.12 to −0.11	Touratier et al. (2016)
	GOL	Modeling	Preindustrial—2001	−0.084 ± 0.001		−0.006 to −0.005	Palmiéri et al. (2015)
	GOL	Shipborne	Preindustrial—2013		−0.075 (S)*	−0.12 (S)*	Hassoun et al. (2015)
	LIG	CANYON-MED	2013–2020		−0.0016 ± 0.016		This study
	LIG	Shipborne	1998–2016	−0.003 ± 0.001	−0.001 ± 0	−0.002 ± 0	Coppola et al. (2020)
	LIG	Mooring	1995–1997, 2013–2015	−0.0022 ± 0.0002 (S)			Merlivat et al. (2018)
	LIG	Shipborne	1995–2011	−0.003 ± 0.001 (S)			Marcellin Yao et al. (2016)

Note. For the area, GOL corresponds to the Gulf of Lion and LIG to the Ligurian Sea. If not specified, pH is on the total scale, (S) refers to pH on the seawater scale, and the asterisk to deltas over the period. Only significant trends are reported in the table.

extent, the 2017–2018 winter event, are visible (i.e., decrease of NO_3^- from 8 to 7.6 μmol kg $^{-1}$ and increase of pH_T from 8.01 to 8.015 in early 2013 or pH_T increase from 8.003 to 8.075 in early 2018, Figure 4). While NO_3^- and $Si(OH)_4$ have similar rates of increase between the two study areas, at depth, PO_4^{3-} increases twice faster in the Ligurian Sea than in the Gulf of Lion (0.0034 and 0.0016 μmol kg^{-1} year^{-1} respectively).

In the OML, C_T increases in both areas with a concomitant pH_T decrease. In intermediate layers, lower A_T, C_T, and higher pH_T are observed in winter than in other seasons. The periodic increase in pH_T is large enough to affect the slope of decrease, but with pH_T reaching similar values by the end of 2020 in both areas. At depth, C_T increases at a similar rate in both areas, while for pH_T the trend is only significant in the Gulf of Lion.

At all depths, the bottle reference data exhibits large variability in both nutrients and carbonate system variables. Even though the bottle data come from a 15 day- 25 km- matchup with the CANYON-MED derived values from Argo floats, they still reflect the inherent spatial variability in biogeochemical variables in each of the two areas.

4. Discussion

4.1. O_2 Evolution With DWF Events

The episodic ventilation of the intermediate and deeper layers by deep convection is a major source of O_2 for these water masses that are propagated in the western Mediterranean Sea through circulation. Tamburini et al. (2013) have shown that the spreading of dense waters from the Gulf of Lion ventilates deep layers, moving south and east, thus affecting areas such as the Ligurian Sea. Ulses et al. (2021) have also demonstrated that the newly formed deep waters flow south and west, which might be the case for highly convective events such as winter 2012–2013. In both areas, surface waters are typically under-saturated in winter (Figure S5 in Supporting Information S1) with the oxygen undersaturation reaching up to 15%, in agreement with the work of Ulses et al. (2021). In spring, because of *in situ* O_2 production during the spring phytoplankton bloom (depending on nutrients supply and deep convection intensity), O_2 is over-saturated (up to 10%) and the surface waters outgas O_2 (Kassis et al., 2016; Wolf et al., 2018). In summer, the over-saturation prevails and is reinforced by thermal stratification. Finally, in autumn, where a phytoplankton bloom is known to occur in the northwestern Mediterranean Sea, Ulses et al. (2021) have shown that respiration exceeds primary production leading to a small under-saturation. In the Gulf of Lion, convection is especially intense due to the strong wind forcings preconditioning the area combined with the cyclonic circulation (Testor et al., 2018). In the Gulf of Lion, annual bottom-reaching convection occurred in winter from 2009 to 2013 (Margirier et al., 2020), ventilating the intermediate waters where the OML is present. The OML in the LIW stems from the long journey from its formation area (Levantine basin) combined with the presence of bacterial communities receiving a flow of organic matter along its journey (especially during bloom and post-bloom periods). These two phenomena lead to intense respiration lowering O_2 concentrations. In winter 2012–2013, mixing reached more than 2,000 m (Figures 2a and 3a) and homogenized the whole water column. The O_2 minimum disappeared and O_2 increased to more than 200 μmol kg^{-1} in intermediate waters. After restratification, the O_2 minimum reformed with a thickness ranging from 200 to 550 m, and values down to 170 μmol kg^{-1}. From 2014 to 2017, the winter convection remained limited to 500 m (Margirier et al., 2020), leading to an increase in temperature and salinity in the intermediate layers. The O_2 concentration also decreased by around 1 μmol kg^{-1} per year in intermediate layers from 2014 to July 2017 (Figures 2a and 3a). In 2018, intense deep convection occurred reaching at least 1,900 m (as captured by the Argo floats), weakening the O_2 minimum (Figures 2a and 3a). From mid-February to the end of March 2018, O_2 in intermediate waters increased from 180 to 200 μmol kg^{-1} in the Ligurian Sea (data from glider POTAME during the MOOSE T00-40 section; https://www.ego-network.org). Consequently, O_2 remained at relatively high values in the intermediate layer (around 175 μmol kg^{-1}) from March 2018 to January 2019 without an O_2 minimum until the last mixing event in winter 2018–2019 as captured by the fixed mooring data (LION and DYFAMED). By the end of 2019, the O_2 minimum had barely reformed with values around 180 μmol kg^{-1} and a core around 600 m.

The detection of the convective events with Argo floats is consistent with previous studies, although Margirier et al. (2020), using the MLD criterion of Houpert et al. (2016), reported a maximum depth of convection of 2,330 m in 2013, which cannot be captured by Argo floats that profile down to 2,000 m. Between 2014 and 2017, Margirier et al. (2020) detected maximum depths reached by winter convection ranging between 420 and 710 m while the Argo floats detected shallower deepenings (500 m at most). This difference is due to the irregularity of the Argo data and the location of the floats relative to the convective area (Figure 1). The 2018 convective event in the Gulf of Lion is a result of multiple Mixed Layer (ML) deepenings (with a cold winter period in 2018–2019) and its effect on the O_2 distribution over the water column appears limited with no ventilation of deep waters as compared to the 2013 DWF event, during which the volume of deep water formed ranged from 1.5×10^{13} m^3 (Coppola et al., 2017) to 5 to 7×10^{13} m^3 (Testor et al., 2018). The difference between the 2012–2013 and 2017–2018 events can be attributed to several factors: (a) the convective surface area estimated by Margirier et al. (2020) is half the surface reported by Houpert et al. (2016) or Testor et al. (2018) for intensive convective years, (b) large-scale to submesoscale structures mixing waters varied between the two events (eddies, SCVs; Bosse et al., 2015, 2016; Testor et al., 2018), and (c) preconditioned states differed. Indeed, from 2009 to 2013, all winter convections reached the bottom, while between 2014 and 2018, in the absence of convection, the

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intermediate layers rapidly evolved to a warmer and saltier state. This led to a thickening of the LIW and thus to a considerable input of salt into the intermediate layers, and an increase in deep stratification below the LIW which, combined with the increase in surface temperature and the evolution of the air-sea heat fluxes constrained the depth reached by convection. It is expected, pending that there are no intense deep convection events, that the increase in LIW temperature and salinity will continue and also be reflected in the subsequent WMDW properties formed by their mixing. This amount of salt in the intermediate layers is a good indication of the future convective state for the following winter (Margirier et al., 2020; Testor et al., 2018). Furthermore, intense mixing is enhanced in winter when LIW isopycnals reach the surface. Thus, surface waters become denser than usual and combined with wind forcing, convection becomes more intense and deeper.In the Ligurian Sea, weaker atmospheric forcings than in the Gulf of Lion lead to episodically occurring convection events (Estournel et al., 2016). In the Ligurian Sea, lacking MLD data due to the limited number of Argo floats in the area was compensated using modeled MLD data around the DYFAMED mooring (Figure 3b). At the end of 2012, the O_2 minimum was vertically spread between 200 and 800 m with a mean concentration of around 165 µmol kg^{-1}. At the beginning of 2013, glider transects from Nice to Calvi captured a strong mixing event with a deepening of the mixed layer to 800 m (Bosse et al., 2017) and modeled MLDs increased to more than 2,000 m (whereas no Argo float were present in the area hindering the retrieval of Argo-derived MLDs). In the following summer, shipborne observations revealed an O_2-enriched (around 195 µmol kg^{-1}) layer between 300 and 1,200 m (Bosse et al., 2017). The O_2 minimum was reformed more than a year later by summer 2014 and its O_2 content decreased from January 2014 by 1 µmol kg^{-1} per year until the convection event of 2018 (Figure 3b). This slow decrease differs from the one reported at the DYFAMED site by Coppola et al. (2018) who reported a decrease of 5 µmol kg^{-1} per year on average over the 1994–2005 period. However, in the period 2007–2014, their results showed a stable concentration of around 180 µmol kg^{-1}. Currently, in the Western basin, oxygen consumption by heterotrophic respiration in the deeper layers has been estimated to be about 0.6 µmol kg^{-1} year^{-1} for the 500–3,500 m depth range (Powley et al., 2016). This is consistent with the idea that the O_2 decrease in the OML (estimated here around 1 µmol kg^{-1} year^{-1}) is mainly dominated by heterotrophic respiration due to some labile DOC (Dissolved Organic Carbon) supply.

In winter 2018, modeled MLD data reveal a mixing event up to 2,000 m with an increase in O_2 up to more than 210 µmol kg^{-1}. This episodic mixing event may also have slowed the decreasing trend in O_2 in the OML as the 2006 intense mixing in the Gulf of Lion (Coppola et al., 2018) is considered to have happened before. With no apparent mixing until the end of our time series, the O_2 minimum remained stable (165 µmol kg^{-1}) and spread from 350 to 800 m by July 2020. In the Ligurian Sea, the high variability in O_2 along the time series (Figures 3 and 4b; Figure S1 in Supporting Information S1) stems from the different locations of the mooring and Argo data. The Argo profiles were mainly located West of Corsica, where a vein of LIW is strongly located with lower O_2 concentrations. In the Ligurian Sea, the 2018 winter was the last cold winter with important heat loss at the beginning of March, inducing mixing up to 1,000 m caught by the DYFAMED mooring or up to 2,000 m as modeled. The ventilation of the OML is especially important as the Mediterranean circulation influences the Atlantic Ocean through the intermediate and deep waters flowing through Gibraltar where changes in temperature, salinity, and O_2 in the outflowing waters could affect the North Atlantic (Schroeder et al., 2016).

In the Ligurian Sea, we estimate a clear O_2 decrease in the OML in the absence of winter mixing, consistent with previous studies (Coppola et al., 2017) and in agreement with the heat and salt increases in the OML over the last decade (Margirier et al., 2020). Conversely, in the Gulf of Lion, winter mixing regularly reaches depth greater than in the Ligurian Sea (Margirier et al., 2020; Testor et al., 2018) therefore ventilating the OML and hindering the detection of O_2 trends. Both physical and biological processes are involved in the strengthening of the OML. The biological processes at that depth depend greatly on the input of DOC (Dissolved Organic Carbon) to heterotrophic organisms, however, this data is lacking. Ulses et al. (2021) have shown that in the northwestern Mediterranean Sea and specifically in the Gulf of Lion, the annual O_2 budget is dominated by air-sea exchanges and physical transport during convective years such as the winter 2012–2013 much more than by biogeochemical activity (with respiration and nitrification from heterotrophic organisms under the euphotic zone estimated at an oxygen consumption of 4 mol m^{-2} year^{-1}).

4.2. Nutrient Dynamics

In the oligotrophic northwestern Mediterranean Sea, one of the only regions where a yearly phytoplankton bloom occurs (Lavigne et al., 2013), winter mixing of the water column induces the upwelling of bioavailable nutrients from deep water masses to the surface (Estrada et al., 2014; Marty & Chiavérini, 2010; Severin et al., 2014; Ulses et al., 2016) and the refueling of the photic layer influencing the intensity of the spring phytoplankton blooms (Lévy et al., 1998; Migon et al., 2002; Ulses et al., 2016). The efficiency of winter vertical convection is a main determinant of the availability of nutrients in surface waters and of phytoplanktonic blooms during the subsequent late spring (Lavigne et al., 2013) and the consecutive export of particulate organic carbon (POC) at depth. However, Macias et al. (2018) projected that, by the year 2030, the main control of primary production in the northwestern Mediterranean Sea may likely change from deep winter convection to a condition where mesoscale activity will have a predominant role for nutrient delivery into the euphotic layer, which could cause phenological changes of planktonic processes. These authors highlight the crucial role of wind forcing on deep convection and preconditioning and, project that the coupling between mesoscale activity and surface currents would become a more important fertilization mechanism than deep convection as the latter weakens with global warming.

At the surface (Figures 4a–4c, Table 1, Figure S3 in Supporting Information S1), no trends were significant. During our study period (2013–2020), nitrate concentrations increased in the OML (Figures 4h–4j) and nutrients increased at depth (Figures 4o–4q) in the Gulf of Lion and at depth in the Ligurian Sea for both nitrates and silicates (Table 1). Specifically, NO_3^-, and $Si(OH)_4$ increased at depth with no significant difference between the two areas (Figures 4o and 4q). In the Ligurian Sea, at the DYFAMED site, Pasqueron de Fommervault, Migon, D′Ortenzio, et al. (2015), over the period 1991–2011, found a significant increase in NO_3^- of 0.23% per year, while $Si(OH)_4$ had no significant trend (Table 1). They also detected an abrupt change in 2005–2006 for NO_3^-, PO_4^{3-}, $Si(OH)_4$, characterized by a slight but statistically significant increase in nutrient concentration linked to the intense winter convection observed in 2005 and in 2006 that led to the formation of new warmer and saltier Western Mediterranean Deep Water (WMDW; Font et al., 2007; López-Jurado et al., 2005; Schröder et al., 2006; Schroeder et al., 2010; Smith et al., 2008). This can be compared to the impact the 2012–2013 DWF event had on nutrients at depth (Figures 4h–4j and 4o–4q), the mixing of enriched deep waters with depleted surface waters causing a large dispersion in nutrients (up to 2, 0.1 and 3 μmol kg^{-1} respectively for NO_3^-, PO_4^{3-} and $Si(OH)_4$) in intermediate and deep waters. The significance of the predictor variables on the significant nutrient trends was also assessed (Text S1 and Table S2 in Supporting Information S1).

The response of nutrients to ML dynamics remains nuanced: to a certain extent, deeper MLDs lead to more efficient transport of nutrients in surface waters. However, Heimbürger et al. (2013) suggested that a succession of ML deepenings, even though of lesser magnitude, can be more efficient than a single one. While our data show increasing trends at depth in both areas with an increase two times larger in the Ligurian Sea than in the Gulf of Lion, Pasqueron de Fommervault, Migon, D′Ortenzio, et al. (2015) found a decrease in PO_4^{3-} at depth of −0.62%/year over the period 1991–2011. However, their study considered the layer from 800 m to the bottom whereas the focus of the present paper is on the layer around 2,000 m. Furthermore, Pasqueron de Fommervault, Migon, D′Ortenzio, et al. (2015) hypothesized that the formation of new warmer and saltier WMDW in 2006 led to the uplift of the old WMDW by several hundreds of meters (Schroeder et al., 2008, 2013), increasing nutrient concentrations over the 800–2,000 m depth range. In the intermediate layer, the increase of nutrients is linked to remineralization along the LIW's path (Schroeder et al., 2020) and the periodic inputs through convective winter events. Moreover, high productivity in the upper layers caused more intense remineralization in the intermediate layers. At the annual scale for 2013, Kessouri et al. (2017), estimated that the DWF area was a sink of NO_3^- and PO_4^{3-} in intermediate layers and a source of organic nitrogen and phosphorus throughout the water column for the surrounding regions through circulation. Below 200 m depth, Pasqueron de Fommervault, Migon, D′Ortenzio, et al. (2015) found no clear seasonal variability in nutrients. In our data, the large scatter of nutrient concentration in the intermediate layer is linked to the spatial distribution of the float profiles (Figure 1) and to the consequences of the mixing events. The nutrient increases in intermediate waters are close to the Redfield's model ($C:N:Si:P:-O_2 = 106:16:15:1:-172$; Pujo-Pay et al., 2011), indicating faster remineralization of NO_3^- than of $Si(OH)_4$ and PO_4^{3-} (Schroeder et al., 2020). Higher N:P ratios in intermediate waters could be a signature of the original eastern Mediterranean waters contributing to its formation (Krom et al., 2005) or of the activity of heterotrophic communities in the Mediterranean mesopelagic layer (Rahav et al., 2019).

The concurrent increase of nutrients in both the OML and at 2,000 m can be the result of many interplaying factors. First, the different evolutions between nutrients led to a significant increase in the N:P ratio at all depths (estimated from the CANYON-MED derived nutrients, data not shown), yielding an increasing P-limitation relative to Redfield's model, consistent with the findings of Pasqueron de Fommervault, Migon, D′Ortenzio, et al. (2015) at DYFAMED. Indeed, the N:P ratio is always high in the atmospheric material (Bartoli et al., 2005; Krishnamurthy et al., 2010; Pasqueron de Fommervault, Migon, Dufour, et al., 2015), and the impact of atmospheric deposition is particularly important in the whole Mediterranean Sea (Christodoulaki et al., 2013; Pasqueron de Fommervault, Migon, Dufour, et al., 2015). This P-limitation increased faster in the Gulf of Lion than in the Ligurian Sea through a decoupling between NO_3^- and PO_4^{3-} trends (nitrates increased while phosphates did not significantly evolve). Second, physical circulation of the water masses in this area may have brought nutrient inputs from the southeast through advection and isopycnal diffusion from the West Corsica current. Third, due to the marked decrease in convection and mixing, water masses might have evolved from a structure with multiple water masses overlapping at the bottom to a more homogeneous monolayer situation. This enables a better detection of nutrient increases in the deep water masses through remineralization processes. O_2 decreased at depth in both the Gulf of Lion and Ligurian Sea, which is consistent with the signature of remineralization caused by higher microbial activity. Fourth, the decrease of local convective events would likely result in weaker replenishment in surface and accumulation of nutrients at depth. In the North Atlantic, Williams and Follows (2003) have shown the accumulation of nitrates at the bottom in the absence of advection. Similarly, in the absence of convection these nutrients are no longer upwelled to the surface and/or diffused through advection.

4.3. Carbonate System Variability

The characteristics of acidification of the Mediterranean Sea are linked to its biogeochemical characteristics and circulation features (Álvarez et al., 2014; Hainbucher et al., 2014). Specifically, it is known to absorb more anthropogenic CO_2 per unit area (Palmiéri et al., 2015) due to the high A_T values (linked to the high salinities of the Mediterranean Sea caused by evaporation) increasing its capacity to absorb but also buffer anthropogenic CO_2. The deep penetration of CO_2 results in pH declines larger than in other areas where deep waters are not ventilated at such short timescales (Schneider et al., 2014). Specifically, carbon sequestration stems from two main causes, the physical and biological pumps, both intricately linked to the intermediate waters (Schroeder et al., 2020). First, the cooling of surface waters increases CO_2 absorption, and during DWF events CO_2-enriched water masses deepen and consequently sequester CO_2 through the physical pump (Cantoni et al., 2016; Touratier et al., 2016). Second, through the biological pump, the uptake of CO_2 during photosynthesis is followed by its release at depth when the sinking organic matter is remineralized, mainly occurring in the intermediate layers (Béthoux et al., 2005). The distribution of pH is a result of the equilibrium between ocean mixing, biological production and remineralization, precipitation and dissolution of calcium carbonate, and temperature and pressure changes across the water column (Lauvset et al., 2020). In the global ocean, the most important natural process controlling pH in the ocean interior is organic matter remineralization (Lauvset et al., 2020). In the Mediterranean Sea, high rates of organic matter remineralization are observed in intermediate and deep waters related to the downward export of dissolved organic carbon (Lefèvre et al., 1996), especially during winter DWF events (Copin-Montégut & Avril, 1993), thus having a large influence on pH. In the intermediate layers, increased respiration and organic matter remineralization also lower pH_T and increase C_T, decreasing the buffering capacity (Álvarez et al., 2014; Urbini et al., 2020).

At the surface, none of the trends for carbonate system variables are significant (Figure S3 in Supporting Information S1). In intermediate waters, our results for C_T and pH_T are similar to estimates by previous studies. However, at depth, the magnitude of the pH trend is two to four times lower than previously described. This difference may be explained by the peculiar location of Argo floats, west of Corsica, for most of our Ligurian Sea profiles. C_T increased twice faster in intermediate waters than previously estimated (Coppola et al., 2020, Table 1) while at depth the results were much more similar. It should be noted that the trends at intermediate depths described by Coppola et al. (2020) spanned over the 300–800 m layer whereas ours focused on the area around the O_2 minimum, therefore covering a smaller vertical portion. The distribution of C_T in the water column is driven by an equilibrium between the biological pump, which lowers C_T at the surface and increases it at intermediate depths, and the physical pump which exchanges CO_2 at the air-sea interface. Strong mixing events episodically bring together intermediate waters with cold surface waters poorer in A_T and C_T, with a higher pH_T and depending on convection strength C_T-enriched deep waters with a lower pH_T as compared to the intermediate waters. The effect is particularly strong on pH_T changing the slope of decrease, but with pH_T reaching similar values by the end of 2020 in both areas.

The large impact of winter mixing on the C_T and pH signal is crucial as it drives the acidification signal. Indeed, pH trends between both areas would be similar were it not for (a) convective events that increase pH in intermediate layers and (b) strong mixing events (such as in 2013 and 2018) that increase pH in the deep layers. Furthermore, Touratier and Goyet (2011) have shown that the deep convection and cascading in the Gulf of Lion could explain the relatively high rate of acidification estimated in the deep layers of the western Mediterranean Sea. Therefore, these convection events seem to induce a slowing down of the acidification process in intermediate waters, essential in weakening the acidification process already reported in the Mediterranean Sea (Hassoun et al., 2015; Palmiéri et al., 2015; Touratier & Goyet, 2011). Álvarez et al. (2014) have shown that the CO_2 chemistry is less sensitive to temperature in the Mediterranean Sea than in the Atlantic because of the low C_T/A_T ratio and high buffer factors. Moreover, they demonstrated that the increase in atmospheric CO_2 increases C_T with little effect on A_T which is consistent with our results with an increase in C_T with no significant change in A_T (Figure 4).

In the Mediterranean Sea, Argo floats, moorings and research cruises provide high-quality biogeochemical data. However, some areas remain undersampled, as for example, the Ligurian Sea at some moments of our study, because of the circulation driving the Argo floats away from the basin. This limitation can be lessened through the use of glider endurance lines at specific locations to improve data coverage. In the northwestern Mediterranean Sea, two glider sections part of the MOOSE network and covering a north-south axis have been providing quality O_2 data but for a short time, thus they were not incorporated in this study.

5. Conclusion

The consequences of climate change on the physical properties of water masses are well established, with warming and salinification of the Levantine Intermediate Water in the northwestern Mediterranean Sea (Margirier et al., 2020) and in the deep waters of the western Mediterranean Sea (Borghini et al., 2014) leading to an increase in stratification and a decrease in the intensity and frequency of dense water formation events (Macias et al., 2018; Somot et al., 2006; Soto-Navarro et al., 2020). This is likely to reduce the ventilation of the water column as an intensification of the O_2 minimum in the intermediate layers is already visible in the Ligurian Sea (Coppola et al., 2018). In the present study, the combination of mooring, Argo, and ship-based observations show that the O_2 minimum is strongly affected by the intermittent convection process. In the absence of deep convection events, the O_2-depleted layer tends to spread vertically and to intensify even more so in the Ligurian Sea, where the mixing events are less regular and intense than in the Gulf of Lion. When these events occur, the O_2 minimum is affected with an increase of O_2 in intermediate layers depending on the intensity of the winter convection, followed by a decrease.

Integrated observing networks and multi-platforms approaches are fundamental in studying dense water formation events (Tintoré et al., 2019) and their impacts on biogeochemistry (monthly and yearly cruises, moorings, Argo floats). The application of the CANYON-MED neural networks (Fourrier et al., 2020, 2021) on the large network of O_2-equipped Argo floats in the northwestern Mediterranean Sea allowed the first study of reconstructed time series of nutrients and carbonate system variables with large spatial and temporal coverage. Nevertheless, they are limited by their technical capacities to a profiling depth of 2,000 m and as drifting platforms, sometimes offer biased representations of the studied areas. We were able to describe how convective events impact nutrients and carbonate system variables changing their overall evolutions over time and at different depths. In the Gulf of Lion, nitrates increase in the Oxygen Minimum Layer at intermediate depths and all nutrients increase at depth, whereas in the Ligurian Sea only nitrates and silicates at depth increase over the period of study. However, the decoupling between nitrates and phosphates might lead to an evolution in the nutrient molar ratios as compared to Redfield's model. Complementary studies are required to further investigate the exact cause of the nutrient increases between the atmospheric, physical, and biological factors interconnected. Finally, long ocean acidification time series of consistent sampling are still lacking for the Mediterranean Sea (The MerMex Group, 2011). Our approach using neural-network derived pH_T allowed for acidification estimates in different layers of the water column. Overall, C_T increased with a concurrent pH_T decrease and were strongly affected by mixing events. This evolution is visible throughout the water column, which could affect the deep marine ecosystem in the near future. In this context, the development of carbonate system regional models becomes essential by coupling both *in situ* observations and neural network predictions.

Data Availability Statement

Argo data are available at http://doi.org/10.17882/42182#89696 or at ftp://ftp.ifremer.fr/ifremer/argo/dac/coriolis. These data were collected and made freely available by the International Argo Program and the national programs that contribute to it (https://argo.ucsd.edu, https://www.ocean-ops.org). The Argo Program is part of the Global Ocean Observing System. This study represents a contribution to the NAOS project (funded by the Agence Nationale de la Recherche in the framework of the French "Equipement d'avenir" program grant ANR J11R107-F).

Acknowledgments
We thank Claude Estournel for the simulation performed using the HPC CALMIP platform under grant P09115. The SYMPHONIE model is distributed by the SIROCCO group (https://sirocco.obs-mip.fr). We also thank Louis Legendre (LOV, SU), Louis Prieur (LOV, SU) and Dominique Lefèvre (MIO) for fruitful discussions about the results and the exploration of hypotheses in our study. We acknowledge the MOOSE program (Mediterranean Ocean Observing System for the Environment) coordinated by CNRS-INSU and the Research Infrastructure ILICO (CNRS-IFREMER). We are thankful to the European Multidisciplinary Seafloor and water-column Observatory (EMSO) European Research Infrastructure Consortium (ERIC) for ensuring long-term, sustained and continuous data streams from the DYFAMED and LION moorings. For seawater sample analyses, we also thank the SNAPO-CO2 at LOCEAN, Sorbonne Université—CNRS, France. Finally, we would like to thank the editors and the reviewers for their suggestions and comments which strongly improved the final version of the paper.

References

Álvarez, M., Sanleón-Bartolomé, H., Tanhua, T., Mintrop, L., Luchetta, A., Cantoni, C., et al. (2014). The CO_2 system in the Mediterranean Sea: A basin wide perspective. *Ocean Science*, *10*(1), 69–92. https://doi.org/10.5194/os-10-69-2014

Aminot, A., & Kérouel, R. (2007). *Dosage automatique des nutriments dans les eaux marines: Méthodes en flux continu*. Editions Quae.

Argo. (2020). Argo float data and metadata from Global Data Assembly Centre (Argo GDAC) [Dataset]. SEANOE. https://doi.org/10.17882/42182

Bartoli, G., Migon, C., & Losno, R. (2005). Atmospheric input of dissolved inorganic phosphorus and silicon to the coastal northwestern Mediterranean Sea: Fluxes, variability and possible impact on phytoplankton dynamics. *Deep Sea Research Part I: Oceanographic Research Papers*, *52*(11), 2005–2016. https://doi.org/10.1016/j.dsr.2005.06.006

Béthoux, J. P., El Boukhary, M. S., Ruiz-Pino, D., Morin, P., & Copin-Montégut, C. (2005). Nutrient, oxygen and carbon ratios, CO_2 sequestrationand anthropogenic forcing in the Mediterranean Sea. In A. Saliot (Ed.), *The Mediterranean Sea* (Vol. 5K, pp. 67–86). Springer Berlin Heidelberg. https://doi.org/10.1007/b107144

Bittig, H. C., Maurer, T. L., Plant, J. N., Schmechtig, C., Wong, A. P. S., Claustre, H., et al. (2019). A BGC-Argo guide: Planning, deployment, data handling and usage. *Frontiers in Marine Science*, *6*, 502. https://doi.org/10.3389/fmars.2019.00502

Borghini, M., Bryden, H., Schroeder, K., Sparnocchia, S., & Vetrano, A. (2014). The Mediterranean is becoming saltier. *Ocean Science*, *10*(4), 693–700. https://doi.org/10.5194/os-10-693-2014

Bosse, A., Testor, P., Houpert, L., Damien, P., Prieur, L., Hayes, D., et al. (2016). Scales and dynamics of Submesoscale Coherent Vortices formed by deep convection in the northwestern Mediterranean Sea. *Journal of Geophysical Research: Oceans*, *121*, 7716–7742. https://doi.org/10.1002/2016JC012144

Bosse, A., Testor, P., Mayot, N., Prieur, L., D'Ortenzio, F., Mortier, L., et al. (2017). A submesoscale coherent vortex in the Ligurian Sea: From dynamical barriers to biological implications. *Journal of Geophysical Research: Oceans*, *122*(8), 6196–6217. https://doi.org/10.1002/2016JC012634

Bosse, A., Testor, P., Mortier, L., Prieur, L., Taillandier, V., d'Ortenzio, F., & Coppola, L. (2015). Spreading of Levantine Intermediate Waters by submesoscale coherent vortices in the northwestern Mediterranean Sea as observed with gliders. *Journal of Geophysical Research: Oceans*, *120*(3), 1599–1622. https://doi.org/10.1002/2014JC010263

Cantoni, C., Luchetta, A., Chiggiato, J., Cozzi, S., Schroeder, K., & Langone, L. (2016). Dense water flow and carbonate system in the southern Adriatic: A focus on the 2012 event. *Marine Geology*, *375*, 15–27. https://doi.org/10.1016/j.margeo.2015.08.013

Christodoulaki, S., Petihakis, G., Kanakidou, M., Mihalopoulos, N., Tsiaras, K., & Triantafyllou, G. (2013). Atmospheric deposition in the Eastern Mediterranean. A driving force for ecosystem dynamics. *Journal of Marine Systems*, *109–110*, 78–93. https://doi.org/10.1016/j.jmarsys.2012.07.007

Copin-Montégut, G., & Avril, B. (1993). Vertical distribution and temporal variation of dissolved organic carbon in the North-Western Mediterranean Sea. *Deep-Sea Research Part I Oceanographic Research Papers*, *40*(10), 1963–1972. https://doi.org/10.1016/0967-0637(93)90041-Z

Coppola, L., Boutin, J., Gattuso, J.-P., Lefèvre, D., & Metzl, N. (2020). The carbonate system in the Ligurian Sea. In *The Mediterranean Sea in the era of global change* (Vol. 1, pp. 79–103). John Wiley & Sons, Ltd. https://doi.org/10.1002/9781119706960.ch4

Coppola, L., & Diamond-Riquier, E. (2008). MOOSE (DYFAMED) [Dataset]. SEANOE. https://doi.org/10.18142/131

Coppola, L., Diamond-Riquier, E., & Carval, T. (2019). Dyfamed observatory data [Dataset]. SEANOE. https://doi.org/10.17882/43749

Coppola, L., Legendre, L., Lefèvre, D., Prieur, L., Taillandier, V., & Diamond-Riquier, E. (2018). Seasonal and inter-annual variations of dissolved oxygen in the northwestern Mediterranean Sea (DYFAMED site). *Progress in Oceanography*, *162*, 187–201. https://doi.org/10.1016/j.pocean.2018.03.001

Coppola, L., Prieur, L., Taupier-Letage, I., Estournel, C., Testor, P., Lefèvre, D., et al. (2017). Observation of oxygen ventilation into deep waters through targeted deployment of multiple Argo-O_2 floats in the north-western Mediterranean Sea in 2013. *Journal of Geophysical Research: Oceans*, *122*(8), 6325–6341. https://doi.org/10.1002/2016JC012594

D'Ortenzio, F., Iudicone, D., de Boyer Montegut, C., Testor, P., Antoine, D., Marullo, S., et al. (2005). Seasonal variability of the mixed layer depth in the Mediterranean Sea as derived from in situ profiles. *Geophysical Research Letters*, *32*(12). https://doi.org/10.1029/2005GL022463

D'Ortenzio, F., Taillandier, V., Claustre, H., Prieur, L. M., Leymarie, E., Mignot, A., et al. (2020). Biogeochemical Argo: The test case of the NAOS Mediterranean Array. *Frontiers in Marine Science*, *7*, 120. https://doi.org/10.3389/fmars.2020.00120

Dickson, A. G. (1990). Standard potential of the reaction: AgCl (s) + $12H_2$ (g) = Ag (s) + HCl (aq), and and the standard acidity constant of the ion HSO_4^- in synthetic sea water from 273.15 to 318.15 K. *Journal of Chemical Thermodynamics*, *22*(2), 113–127. https://doi.org/10.1016/0021-9614(90)90074-z

Dickson, A. G., & Goyet, C. (1994). *Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water. Version 2 (No. ORNL/CDIAC-74)*. Oak Ridge National Laboratory. https://doi.org/10.2172/10107773

Dickson, A. G., & Millero, F. J. (1987). A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. *Deep-Sea Research*, *34*(10), 1733–1743. https://doi.org/10.1016/0198-0149(87)90021-5

Dickson, A. G., Sabine, C. L., & Christian, J. R. (2007). *Guide to best practices for ocean CO_2 measurements (Report)*. North Pacific Marine Science Organization. Retrieved from https://repository.oceanbestpractices.org/handle/11329/249

Durrieu De Madron, X., Ramondenc, S., Berline, L., Houpert, L., Bosse, A., Martini, S., et al. (2017). Deep sediment resuspension and thick nepheloid layer generation by open-ocean convection. *Journal of Geophysical Research: Oceans*, *122*(3), 2291–2318. https://doi.org/10.1002/2016JC012062

Edmond, J. M. (1970). High precision determination of titration alkalinity and total carbon dioxide content of sea water by potentiometric titration. *Deep-Sea Research and Oceanographic Abstracts*, *17*(4), 737–750. https://doi.org/10.1016/0011-7471(70)90038-0

Estournel, C., Testor, P., Damien, P., D'Ortenzio, F., Marsaleix, P., Conan, P., et al. (2016). High resolution modeling of dense water formation in the north-western Mediterranean during winter 2012–2013. *Journal of Geophysical Research: Oceans*, *121*(7), 5367–5392. https://doi.org/10.1002/2016JC011935

Estrada, M., Latasa, M., Emelianov, M., Gutiérrez-Rodríguez, A., Fernández-Castro, B., Isern-Fontanet, J., et al. (2014). Seasonal and mesoscale variability of primary production in the deep winter-mixing region of the NW Mediterranean. *Deep-Sea Research Part I Oceanographic Research Papers*, *94*, 45–61. https://doi.org/10.1016/j.dsr.2014.08.003

Font, J., Puig, P., Salat, J., Palanques, A., & Emelianov, M. (2007). Sequence of hydrographic changes in NW Mediterranean deep water due to the exceptional winter of 2005. *Scientia Marina*, *71*(2), 339–346. https://doi.org/10.3989/scimar.2007.71n2339

Fourrier, M., Coppola, L., Claustre, H., D'Ortenzio, F., Sauzède, R., & 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. *Frontiers in Marine Science*, *7*. https://doi.org/10.3389/fmars.2020.00620

Fourrier, M., Coppola, L., Claustre, H., D'Ortenzio, F., Sauzède, R., & Gattuso, J.-P. (2021). Corrigendum: A regional neural network approach to estimate water-column nutrient concentrations and carbonate system variables in the Mediterranean Sea: CANYON-MED. *Frontiers in Marine Science*, *8*, 650509. https://doi.org/10.3389/fmars.2021.650509

Hainbucher, D., Rubino, A., Cardin, V., Tanhua, T., Schroeder, K., & Bensi, M. (2014). Hydrographic situation during cruise M84/3 and P414 (spring 2011) in the Mediterranean Sea. *Ocean Science*, *10*(4), 669–682. https://doi.org/10.5194/os-10-669-2014

Hassoun, A. E. R., Gemayel, E., Krasakopoulou, E., Goyet, C., Abboud-Abi Saab, M., Guglielmi, V., et al. (2015). Acidification of the Mediterranean Sea from anthropogenic carbon penetration. *Deep-Sea Research Part I Oceanographic Research Papers*, *102*, 1–15. https://doi.org/10.1016/j.dsr.2015.04.005

Heimbürger, L.-E., Lavigne, H., Migon, C., D'Ortenzio, F., Estournel, C., Coppola, L., & Miquel, J.-C. (2013). Temporal variability of vertical export flux at the DYFAMED time-series station (Northwestern Mediterranean Sea). *Progress in Oceanography*, *119*, 59–67. https://doi.org/10.1016/j.pocean.2013.08.005

Herrmann, M., Sevault, F., Beuvier, J., & Somot, S. (2010). What induced the exceptional 2005 convection event in the northwestern Mediterranean basin? Answers from a modeling study. *Journal of Geophysical Research*, *115*(C12). https://doi.org/10.1029/2010JC006162

Herrmann, M., Somot, S., Sevault, F., Estournel, C., & Déqué, M. (2008). Modeling the deep convection in the northwestern Mediterranean Sea using an eddy-permitting and an eddy-resolving model: Case study of winter 1986–1987. *Journal of Geophysical Research*, *113*(C4), C04011. https://doi.org/10.1029/2006JC003991

Houpert, L., Durrieu de Madron, X., Testor, P., Bosse, A., D'Ortenzio, F., Bouin, M. N., et al. (2016). Observations of open-ocean deep convection in the northwestern Mediterranean Sea: Seasonal and interannual variability of mixing and deep water masses for the 2007-2013 Period. *Journal of Geophysical Research: Oceans*, *121*(11), 8139–8171. https://doi.org/10.1002/2016JC011857

Kassis, D., Krasakopoulou, E., Korres, G., Petihakis, G., & Triantafyllou, G. S. (2016). Hydrodynamic features of the South Aegean Sea as derived from Argo T/S and dissolved oxygen profiles in the area. *Ocean Dynamics*, *66*(11), 1449–1466. https://doi.org/10.1007/s10236-016-0987-2

Kessouri, F., Ulses, C., Estournel, C., Marsaleix, P., D'Ortenzio, F., Severin, T., et al. (2018). Vertical mixing effects on phytoplankton dynamics and organic carbon export in the western Mediterranean Sea. *Journal of Geophysical Research: Oceans*, *123*(3), 1647–1669. https://doi.org/10.1002/2016JC012669

Kessouri, F., Ulses, C., Estournel, C., Marsaleix, P., Severin, T., Pujo-Pay, M., et al. (2017). Nitrogen and phosphorus budgets in the Northwestern Mediterranean deep convection region. *Journal of Geophysical Research: Oceans*, *122*(12), 9429–9454. https://doi.org/10.1002/2016JC012665

Krishnamurthy, A., Moore, J. K., Mahowald, N., Luo, C., & Zender, C. S. (2010). Impacts of atmospheric nutrient inputs on marine biogeochemistry. *Journal of Geophysical Research*, *115*(G1), G01006. https://doi.org/10.1029/2009JG001115

Krom, M. D., Woodward, E. M. S., Herut, B., Kress, N., Carbo, P., Mantoura, R. F. C., et al. (2005). Nutrient cycling in the south east Levantine basin of the eastern Mediterranean: Results from a phosphorus starved system. *Deep-Sea Research Part II Topical Studies in Oceanography*, *52*(22–23), 2879–2896. https://doi.org/10.1016/j.dsr2.2005.08.009

Lascaratos, A., Williams, R. G., & Tragou, E. (1993). A mixed-layer study of the formation of Levantine intermediate water. *Journal of Geophysical Research*, *98*(C8), 14739–14749. https://doi.org/10.1029/93JC00912

Lauvset, S. K., Carter, B. R., Pèrez, F. F., Jiang, L.-Q., Feely, R. A., Velo, A., & Olsen, A. (2020). Processes driving global interior ocean pH distribution. *Global Biogeochemical Cycles*, *34*(1), e2019GB006229. https://doi.org/10.1029/2019GB006229

Lavigne, H., D'Ortenzio, F., Migon, C., Claustre, H., Testor, P., d'Alcalà, M. R., et al. (2013). Enhancing the comprehension of mixed layer depth control on the Mediterranean phytoplankton phenology. *Journal of Geophysical Research: Oceans*, *118*(7), 3416–3430. https://doi.org/10.1002/jgrc.20251

Lefèvre, D., Denis, M., Lambert, C. E., & Miquel, J.-C. (1996). Is DOC the main source of organic matter remineralization in the ocean water column? *Journal of Marine Systems*, *7*(2), 281–291. https://doi.org/10.1016/0924-7963(95)00003-8

Le Traon, P.-Y., D'Ortenzio, F., Babin, M., Leymarie, E., Marec, C., Pouliquen, S., et al. (2020). Preparing the new phase of Argo: Scientific achievements of the NAOS project. *Frontiers in Marine Science*, *7*, 577408. https://doi.org/10.3389/fmars.2020.577408

Lévy, M., Mémery, L., & Madec, G. (1998). The onset of a bloom after deep winter convection in the northwestern Mediterranean Sea: Mesoscale process study with a primitive equation model. *Journal of Marine Systems*, *16*(1), 7–21. https://doi.org/10.1016/S0924-7963(97)00097-3

Lewis, E., Wallace, D. W. R., & Allison, L. J. (1998). *Program developed for CO_2 system calculations. ORNL/CDIAC-105*. Carbon Dioxide Information Analysis Center; Oak Ridge National Laboratory; U.S. Department of Energy. https://doi.org/10.3334/CDIAC/otg.CO2SYS_DOS_CDIAC105

López-Jurado, J.-L., González-Pola, C., & Vélez-Belchí, P. (2005). Observation of an abrupt disruption of the long-term warming trend at the Balearic Sea, western Mediterranean Sea, in summer 2005. *Geophysical Research Letters*, *32*(24), L24606. https://doi.org/10.1029/2005GL024430

Macias, D., Garcia-Gorriz, E., & Stips, A. (2018). Deep winter convection and phytoplankton dynamics in the NW Mediterranean Sea under present climate and future (horizon 2030) scenarios. *Scientific Reports*, *8*(1), 6626. https://doi.org/10.1038/s41598-018-24965-0

Marcellin Yao, K., Marcou, O., Goyet, C., Guglielmi, V., Touratier, F., & Savy, J.-P. (2016). Time variability of the north-western Mediterranean Sea pH over 1995–2011. *Marine Environmental Research*, *116*, 51–60. https://doi.org/10.1016/j.marenvres.2016.02.016

Margirier, F. (2018). *Etude de la variabilité physique et biogéochimique des masses d'eaux en Mer Méditerranée*. Sorbonne Université.

Margirier, F., Testor, P., Heslop, E., Mallil, K., Bosse, A., Houpert, L., et al. (2020). Abrupt warming and salinification of intermediate waters interplays with decline of deep convection in the Northwestern Mediterranean Sea. *Scientific Reports*, *10*(1), 20923. https://doi.org/10.1038/s41598-020-77859-5

Marsaleix, P., Auclair, F., Floor, J. W., Herrmann, M. J., Estournel, C., Pairaud, I., & Ulses, C. (2008). Energy conservation issues in sigma-coordinate free-surface ocean models. *Ocean Modelling*, *20*, 61–89. https://doi.org/10.1016/j.ocemod.2007.07.005

Marty, J. C., & Chiavérini, J. (2010). Hydrological changes in the Ligurian Sea (NW Mediterranean, DYFAMED site) during 1995–2007 and biogeochemical consequences. *Biogeosciences*, *7*(7), 2117–2128. https://doi.org/10.5194/bg-7-2117-2010

Marty, J.-C., Chiavérini, J., Pizay, M.-D., & Avril, B. (2002). Seasonal and interannual dynamics of nutrients and phytoplankton pigments in the western Mediterranean Sea at the DYFAMED time-series station (1991–1999). *Deep-Sea Research Part II Topical Studies in Oceanography*, *49*(11), 1965–1985. https://doi.org/10.1016/S0967-0645(02)00022-X

Mayot, N., D'Ortenzio, F., Taillandier, V., Prieur, L., de Fommervault, O. P., Claustre, H., et al. (2017). Physical and biogeochemical controls of the phytoplankton blooms in North Western Mediterranean Sea: A Multiplatform approach over a complete annual cycle (2012-2013 DEWEX Experiment). *Journal of Geophysical Research: Oceans*, *122*(12), 9999–10019. https://doi.org/10.1002/2016JC012052

Mehrbach, C., Culberson, C. H., Hawley, J. E., & Pytkowicx, R. M. (1973). Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limnology & Oceanography*, *18*(6), 897–907. https://doi.org/10.4319/lo.1973.18.6.0897

Merlivat, L., Boutin, J., Antoine, D., Beaumont, L., Golbol, M., & Vellucci, V. (2018). Increase of dissolved inorganic carbon and decrease in pH in near-surface waters in the Mediterranean Sea during the past two decades. *Biogeosciences*, 5653–5662. https://doi.org/10.5194/bg-15-5653-2018

Migon, C., Sandroni, V., Marty, J.-C., Gasser, B., & Miquel, J.-C. (2002). Transfer of atmospheric matter through the euphotic layer in the northwestern Mediterranean: Seasonal pattern and driving forces. *Deep-Sea Research Part II Topical Studies in Oceanography*, *49*(11), 2125–2141. https://doi.org/10.1016/S0967-0645(02)00031-0

Millot, C. (1999). Circulation in the western Mediterranean Sea. *Journal of Marine Systems*, *20*(1), 423–442. https://doi.org/10.1016/S0924-7963(98)00078-5

Millot, C., & Taupier-Letage, I. (2005). Circulation in the Mediterranean Sea. In A. Saliot (Ed.), *The Mediterranean Sea* (Vol. 5K, pp. 29–66). Springer Berlin Heidelberg. https://doi.org/10.1007/b107143

Moutin, T., & Raimbault, P. (2002). Primary production, carbon export and nutrients availability in western and eastern Mediterranean Sea in early summer 1996 (MINOS cruise). *Journal of Marine Systems*, *33*(34), 273–288. https://doi.org/10.1016/S0924-7963(02)00062-3

Niewiadomska, K., Claustre, H., Prieur, L., & d'Ortenzio, F. (2008). Submesoscale physical-biogeochemical coupling across the Ligurian current (northwestern Mediterranean) using a bio-optical glider. *Limnology & Oceanography*, *53*(5part2), 2210–2225. https://doi.org/10.4319/lo.2008.53.5_part_2.2210

Packard, T. T., Minas, H. J., Coste, B., Martinez, R., Bonin, M. C., Gostan, J., et al. (1988). Formation of the Alboran oxygen minimum zone. *Deep-Sea Research, Part A: Oceanographic Research Papers*, *35*(7), 1111–1118. https://doi.org/10.1016/0198-0149(88)90003-9

Pagès, R., Baklouti, M., Barrier, N., Richon, C., Dutay, J.-C., & Moutin, T. (2020). Changes in rivers inputs during the last decades significantly impacted the biogeochemistry of the eastern Mediterranean basin: A modelling study. *Progress in Oceanography*, *181*, 102242. https://doi.org/10.1016/j.pocean.2019.102242

Palmiéri, J., Orr, J. C., Dutay, J.-C., Béranger, K., Schneider, A., Beuvier, J., & Somot, S. (2015). Simulated anthropogenic CO_2 storage and acidification of the Mediterranean Sea. *Biogeosciences*, *12*(3), 781–802. https://doi.org/10.5194/bg-12-781-2015

Pasqueron de Fommervault, O., Migon, C., D'Ortenzio, F., Ribera d'Alcalà, M., & Coppola, L. (2015). Temporal variability of nutrient concentrations in the northwestern Mediterranean sea (DYFAMED time-series station). *Deep-Sea Research Part I Oceanographic Research Papers*, *100*, 1–12. https://doi.org/10.1016/j.dsr.2015.02.006

Pasqueron de Fommervault, O., Migon, C., Dufour, A., D'Ortenzio, F., Kessouri, F., Raimbault, P., et al. (2015). Atmospheric input of inorganic nitrogen and phosphorus to the Ligurian Sea: Data from the Cap Ferrat coastal time-series station. *Deep-Sea Research Part I Oceanographic Research Papers*, *106*, 116–125. https://doi.org/10.1016/j.dsr.2015.08.010

Pinardi, N., Cessi, P., Borile, F., & Wolfe, C. L. P. (2019). The Mediterranean Sea overturning circulation. *Journal of Physical Oceanography*, *49*(7), 1699–1721. https://doi.org/10.1175/JPO-D-18-0254.1

Powley, H. R., Krom, M. D., & Van Cappellen, P. (2016). Circulation and oxygen cycling in the Mediterranean Sea: Sensitivity to future climate change. *Journal of Geophysical Research: Oceans*, *121*(11), 8230–8247. https://doi.org/10.1002/2016JC012224

Pujo-Pay, M., Conan, P., Oriol, L., Cornet-Barthaux, V., Falco, C., Ghiglione, J.-F., et al. (2011). Integrated survey of elemental stoichiometry (C, N, P) from the western to eastern Mediterranean Sea. *Biogeosciences*, *8*(4), 883–899. https://doi.org/10.5194/bg-8-883-2011

Rahav, E., Silverman, J., Raveh, O., Hazan, O., Rubin-Blum, M., Zeri, C., et al. (2019). The deep water of Eastern Mediterranean Sea is a hotspot for bacterial activity. *Deep-Sea Research Part II Topical Studies in Oceanography*, *164*, 135–143. https://doi.org/10.1016/j.dsr2.2019.03.004

Reale, M., Giorgi, F., Solidoro, C., Di Biagio, V., Di Sante, F., Mariotti, L., et al. (2020). The regional Earth system model RegCM-ES: Evaluation of the Mediterranean climate and marine biogeochemistry. *Journal of Advances in Modeling Earth Systems*, *12*(9). https://doi.org/10.1029/2019MS001812

Schneider, A., Tanhua, T., Roether, W., & Steinfeldt, R. (2014). Changes in ventilation of the Mediterranean Sea during the past 25 year. *Ocean Science*, *10*(1), 1–16. https://doi.org/10.5194/os-10-1-2014

Schröder, K., Gasparini, G. P., Tangherlini, M., & Astraldi, M. (2006). Deep and intermediate water in the western Mediterranean under the influence of the eastern Mediterranean transient. *Geophysical Research Letters*, *33*(21), L21607. https://doi.org/10.1029/2006GL027121

Schroeder, K., Chiggiato, J., Bryden, H. L., Borghini, M., & Ben Ismail, S. (2016). Abrupt climate shift in the Western Mediterranean Sea. *Scientific Reports*, *6*(1), 23009. https://doi.org/10.1038/srep23009

Schroeder, K., Cozzi, S., Belgacem, M., Borghini, M., Cantoni, C., Durante, S., et al. (2020). Along-path evolution of biogeochemical and carbonate system properties in the intermediate water of the Western Mediterranean. *Frontiers in Marine Science*, *7*, 375. https://doi.org/10.3389/fmars.2020.00375

Schroeder, K., Josey, S. A., Herrmann, M., Grignon, L., Gasparini, G. P., & Bryden, H. L. (2010). Abrupt warming and salting of the Western Mediterranean Deep Water after 2005: Atmospheric forcings and lateral advection. *Journal of Geophysical Research*, *115*(C8), C08029. https://doi.org/10.1029/2009JC005749

Schroeder, K., Lafuente, J., Josey, S., Artale, V., Buongiorno Nardelli, B., Gacic, M., et al. (2012). Circulation of the Mediterranean Sea and its variability. In *The Mediterranean climate: From past to future*.

Schroeder, K., Millot, C., Bengara, L., Ben Ismail, S., Bensi, M., Borghini, M., et al. (2013). Long-term monitoring programme of the hydrological variability in the Mediterranean Sea: A first overview of the HYDROCHANGES network. *Ocean Science*, *9*(2), 301–324. https://doi.org/10.5194/os-9-301-2013

Schroeder, K., Taillandier, V., Vetrano, A., & Gasparini, G. P. (2008). The circulation of the western Mediterranean Sea in spring 2005 as inferred from observations and from model outputs. *Deep-Sea Research Part I Oceanographic Research Papers*, *55*(8), 947–965. https://doi.org/10.1016/j.dsr.2008.04.003

Severin, T., Conan, P., Durrieu de Madron, X., Houpert, L., Oliver, M. J., Oriol, L., et al. (2014). Impact of open-ocean convection on nutrients, phytoplankton biomass and activity. *Deep-Sea Research Part I Oceanographic Research Papers*, *94*, 62–71. https://doi.org/10.1016/j.dsr.2014.07.015

Smith, R. O., Bryden, H. L., & Stansfield, K. (2008). Observations of new western Mediterranean deep water formation using Argo floats 2004–2006. *Ocean Science*, *4*(2), 133–149. https://doi.org/10.5194/os-4-133-2008

Somot, S., Houpert, L., Sevault, F., Testor, P., Bosse, A., Taupier-Letage, I., et al. (2018). Characterizing, modelling and understanding the climate variability of the deep water formation in the North-Western Mediterranean Sea. *Climate Dynamics*, *51*(3), 1179–1210. https://doi.org/10.1007/s00382-016-3295-0

Somot, S., Sevault, F., & Déqué, M. (2006). Transient climate change scenario simulation of the Mediterranean Sea for the twenty-first century using a high-resolution ocean circulation model. *Climate Dynamics*, *27*(7–8), 851–879. https://doi.org/10.1007/s00382-006-0167-z

Soto-Navarro, J., Jordá, G., Amores, A., Cabos, W., Somot, S., Sevault, F., et al. (2020). Evolution of Mediterranean Sea water properties under climate change scenarios in the Med-CORDEX ensemble. *Climate Dynamics*, *54*(3–4), 2135–2165. https://doi.org/10.1007/s00382-019-05105-4

Sournia, A. (1973). La production primaire planctonique en Méditerranée. Essai de mise à jour. In *La production primaire planctonique en Mediterranee. Essai de mise a jour* (pp. 1–128).

Sparnocchia, S., Manzella, G. M. R., & Violette, P. E. L. (1994). The interannual and seasonal variability of the MAW and LIW core properties in the Western Mediterranean Sea. In *Seasonal and interannual variability of the Western Mediterranean Sea* (pp. 177–194). American Geophysical Union (AGU). https://doi.org/10.1029/CE046p0117

Tamburini, C., Canals, M., Durrieu de Madron, X., Houpert, L., Lefèvre, D., Martini, S., et al. (2013). Deep-sea bioluminescence blooms after dense water formation at the ocean surface. *PLoS One*, *8*(7), e67523. https://doi.org/10.1371/journal.pone.0067523

Tanhua, T., Hainbucher, D., Schroeder, K., Cardin, V., Álvarez, M., & Civitarese, G. (2013). The Mediterranean Sea system: A review and an introduction to the special issue. *Ocean Science*, *9*(5), 789–803. https://doi.org/10.5194/os-9-789-2013

Testor, P., Bosse, A., Houpert, L., Margirier, F., Mortier, L., Legoff, H., et al. (2018). Multiscale observations of deep convection in the northwestern Mediterranean Sea during winter 2012–2013 using multiple platforms. *Journal of Geophysical Research: Oceans*, *123*(3), 1745–1776. https://doi.org/10.1002/2016JC012671

Testor, P., Durrieu De Madron, X., Mortier, L., D'Ortenzio, F., Legoff, H., Dausse, D., et al. (2020). LION observatory data [Data set]. SEANOE. https://doi.org/10.17882/44411

The MerMex Group, Durrieu de Madron, X., Guieu, C., Sempéré, R., Conan, P., Cossa, D., et al. (2011). Marine ecosystems' responses to climatic and anthropogenic forcings in the Mediterranean. *Progress in Oceanography*, *91*(2), 97–166. https://doi.org/10.1016/j.pocean.2011.02.003

Tintoré, J., Pinardi, N., Álvarez-Fanjul, E., Aguiar, E., Álvarez-Berastegui, D., Bajo, M., et al. (2019). Challenges for sustained observing and forecasting systems in the Mediterranean Sea. *Frontiers in Marine Science*, *6*, 568. https://doi.org/10.3389/fmars.2019.00568

Touratier, F., & Goyet, C. (2011). Impact of the eastern Mediterranean transient on the distribution of anthropogenic CO_2 and first estimate of acidification for the Mediterranean Sea. *Deep-Sea Research Part I Oceanographic Research Papers*, *58*(1), 1–15. https://doi.org/10.1016/j.dsr.2010.10.002

Touratier, F., Goyet, C., Houpert, L., de Madron, X. D., Lefèvre, D., Stabholz, M., & Guglielmi, V. (2016). Role of deep convection on anthropogenic CO_2 sequestration in the Gulf of Lions (northwestern Mediterranean Sea). *Deep-Sea Research Part I Oceanographic Research Papers*, *113*, 33–48. https://doi.org/10.1016/j.dsr.2016.04.003

Ulses, C., Auger, P.-A., Soetaert, K., Marsaleix, P., Diaz, F., Coppola, L., et al. (2016). Budget of organic carbon in the North-Western Mediterranean open sea over the period 2004–2008 using 3-D coupled physical-biogeochemical modeling. *Journal of Geophysical Research: Oceans*, *121*(9), 7026–7055. https://doi.org/10.1002/2016JC011818

Ulses, C., Estournel, C., Fourrier, M., Coppola, L., Kessouri, F., Lefèvre, D., & Marsaleix, P. (2021). Oxygen budget of the north-western Mediterranean deep-convection region. *Biogeosciences*, *18*(3), 937–960. https://doi.org/10.5194/bg-18-937-2021

Uppström, L. R. (1974). The boron/chlorinity ratio of deep-sea water from the Pacific Ocean. *Deep-Sea Research*, *21*(2), 161–162. https://doi.org/10.1016/0011-7471(74)90074-6

Urbini, L., Ingrosso, G., Djakovac, T., Piacentino, S., & Giani, M. (2020). Temporal and spatial variability of the CO_2 system in a riverine influenced area of the Mediterranean Sea, the northern Adriatic. *Frontiers in Marine Science*, *7*. https://doi.org/10.3389/fmars.2020.00679

van Heuven, S., Pierrot, D., Rae, J., Lewis, E., & Wallace, D. W. R. (2011). *CO2SYS v 1.1, MATLAB program developed for CO_2 system calculations* [Software]. *ORNL/CDIAC-105b*. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy.

Williams, R. G., & Follows, M. J. (2003). Physical transport of nutrients and the maintenance of biological production. In M. J. R. Fasham (Ed.), *Ocean biogeochemistry: The role of the ocean carbon cycle in global change* (pp. 19–51). Springer. https://doi.org/10.1007/978-3-642-55844-3_3

Wolf, M. K., Hamme, R. C., Gilbert, D., Yashayaev, I., & Thierry, V. (2018). Oxygen saturation surrounding deep water formation events in the Labrador Sea from Argo-O2 data. *Global Biogeochemical Cycles*, *32*(4), 635–653. https://doi.org/10.1002/2017GB005829