

Hydrological and Biogeochemical Patterns in the Sicily Channel: New Insights From the Last Decade (2010-2020)

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Placenti F, Torri M, Pessini F, Patti B, Tancredi V, Cuttitta A, Giaramita L, Tranchida G and Sorgente R (2022) Hydrological and Biogeochemical Patterns in the Sicily Channel: New Insights From the Last Decade (2010-2020). Front. Mar. Sci. 9:733540. doi: 10.3389/fmars.2022.733540 The hydrological and biogeochemical time series from 2010 to 2020 have highlighted specific relationships and trends in oceanographic processes and nutrient patterns in the Sicily Channel. Specifically, temperature and salinity time series in the intermediate waters showed a sharp annual increase of about 0.06°C and 0.09 within the period 2010-2020, at rates that are about 50% higher than what observed within the previous decade. Similar trends were also present in deep waters, although with lower variations of both temperature and salinity. The time series in the intermediate water, also highlighted the presence of quasi cyclic fluctuations that can be associated with the alternation of the circulation modes (cyclonic and anticyclonic) of the Northern Ionian Gyre. Moreover, an opposite trend emerged by comparing the nutrients and salinity time series in intermediate waters, while similar patterns has been evidenced between nutrients and chlorophyll-a concentration. This latter finding is not consistently present in the Mediterranean area, suggesting the need of further studies on a wider scale.

Keywords: hydrological patterns, interannual variability, biogeochemical patterns, Sicily Channel, Mediterranean Sea

INTRODUCTION

The Mediterranean Sea (MS) consists of two basins, the Western Mediterranean (WMS) and the Eastern Mediterranean (EMS), connected by the Sicily Channel (SC), and is characterized by a limited water exchange with the Atlantic Ocean. In the MS the net evaporation exceeds the precipitation, driving an anti-estuarine circulation through the Strait of Gibraltar, which has important implications on the physical and biogeochemical properties of the MS. The thermohaline circulation of the MS is described as an open basin-wide cell, which involves the gradual salinification of the fresher surface Atlantic water (AW) while propagating eastward (Gačić et al., 2013), and its transformation into intermediate water (IW), called Levantine Intermediate Water (LIW) or Cretan Intermediate Water (CIW), depending on the specific formation area (Levantine or Cretan Sea, CS). IW spreads westward

and its core is identifiable in the whole MS by a subsurface salinity maximum (S_{max}, Schroeder et al., 2017). It flows into the Ionian Sea (IS), with a significant flow northward to the Adriatic Sea (AdS), and constitutes an important preconditioning agent for the formation of both the Adriatic deep water (AdDW) and Mediterranean deep waters (eastern, EMDW and western, WMDW) (e.g. Roether et al., 1996; Gačić et al., 2013). Some authors have highlighted the presence of two main modes of circulation (cyclonic and anticyclonic) of the North Ionian Gyre (NIG), interpreted in terms of internal processes (e.g. Borzelli et al., 2009; Gačić et al., 2010; Gačić et al., 2011; Gačić et al., 2014; Theocharis et al., 2014), which, alternating on a multiannual scale, operate a different redistribution of heat and salt in the central and Levantine area of the MS. Furthermore, the quasi decadal reversal of the NIG influences the strength of the Mid-Ionian Jet (MIJ; Robinson et al., 2001) and generates cascading repercussions on the physical and chemical characteristics of the water masses in the EMS, as well as in the SC and in the WMS (Menna et al., 2019). A process to explain such reversal is a feedback mechanism, named Adriatic-Ionian Bimodal Oscillation System _BIOS_ (Civitarese et al., 2010; Gačić et al., 2010), driven by the difference in salinity between the saltier and warmer waters originating from EMS (LIW and Levantine Surface Water, LSW_), and the less saline AW entering from the SC (Gačić et al., 2011; Gačić et al., 2014). Briefly, an anticyclonic phase (1993-1997 and 2006-2010) inhibits the AW advection (weakening the MIJ) to the southern Levantine basin and favours the production of salty and warm LIW/CIW. Conversely, a cyclonic phase (1998-2005) favoring the AW advection (strengthening the MIJ) to the southern Levantine Basin, leads to a stronger dilution in the EMS (Schroeder et al., 2017 and internal references). In particular, the anticyclonic mode represents a preconditioning mechanism for the dense-water formation processes in the Aegean Sea and eventually for Eastern Mediterranean Transient (EMT) like events (Demirov and Pinardi, 2002; Gačić et al., 2011). During these events it has been showed that, under favourable conditions, the dense water formation area can switch from the AdS to the CS, with a consequent change of the Eastern Mediterranean Deep Waters (EMDW) properties and a repercussion on the entire thermohaline cell (e.g. Gačić et al., 2013). The effects related to EMT and BIOS also show that the MS is not in a steady-state and that in the last decades it has been affected by a continuous increase in temperature and salinity (e.g. Lacombe et al., 1985; Rixen et al., 2005; Millot, 2007; Borghini et al., 2014; Schroeder et al., 2017), probably due to the effects associated with global warming. Salinity and temperature positive trends, especially in the IW, also show a specific interannual variability (e.g. Gasparini et al., 2005; Gačić et al., 2013; Bonanno et al., 2014; Schroeder et al., 2017), whose effects migrate from one to another basin and can be observed mainly in the SC with a time delay respect to the formation period of about 8 years, based on the data of the transient tracer (Roether et al., 1998), or 10-13 years on the basis of the salinity anomalies (Gačić et al., 2013). In this context, the SC can be considered as a key point for the comprehension of the phenomena underlying the thermohaline circulation at basin scale, as well as of the effects of this variability on the

biogeochemical characteristics of the water masses that pass through it.

Biogeochemically, the MS is an oligotrophic basin despite being almost entirely surrounded by land with high nutrient loadings (e.g. Béthoux et al., 1998; Krom et al., 2004) derived from a large coastal population. The main source of dissolved organic phosphorus (P) and nitrogen (N) entering the WMS and EMS, primarily via the Straits of Gibraltar and Sicily, are mineralized to phosphate (PO_4) and nitrate (NO_3) and subsequently exported out of the basin by the prevailing antiestuarine circulation (e.g. Powley et al., 2017). The very low productivity of the MS is therefore linked both to the antiestuarine circulation (Krom et al., 2010) and to the chemical speciation of the dissolved P and N. They in fact reflects a switch from less bioavailable chemical forms of P and N entering the MS to more bioavailable forms leaving the MS (Powley et al., 2017). The anti-estuarine circulation also contributes to the higher primary productivity of the WMS respect to the EMS, as it acts on the lateral transport of dissolved inorganic nutrients in the deeper water, from the EMS to the WMS. It follows that deep waters (DW) of the WMS are characterized by higher NO₃ and PO₄ concentrations than those of the EMS (e.g. Ribera D'Alcalà et al., 2003) and carried up through upwelling phenomena in the photic zone. Another peculiarity of the MS is the higher molar NO₃:PO₄ DW ratios (21:1 on average in the WMS to 29:1 within the EMS, Ribera D'Alcalà et al., 2003) respect to the global ocean (N:P=16:1, Redfield et al., 1963). The debate on the anomaly of this peculiarity is still open, although recent analysis suggest that for the EMS, the high N:P ratio of the external inputs, together with very limited denitrification (Krom et al., 2010; Huertas et al., 2012; Van Cappellen et al., 2014), explains the very high NO₃: PO₄ DW ratio (Powley et al., 2017).

The aim of this study is to examine the interannual variability of thermohaline and biogeochemical properties of the water masses flowing through the SC in summer during the period since 2010 to 2020. We analyzed the potential mechanism controlling the long-term variability of the water masses properties and evaluated the impact on nutrient concentrations and on the productivity of the marine ecosystem.

DATASET AND METHODS

Oceanographic data have been acquired over 10 oceanographic surveys (named Bansic) carried out in the SC during the summer period from 2010 to 2020 (except for year 2019) aboard the Urania, Minerva Uno and Dallaporta vessels (**Figure 1** and **Table 1**). For this study, *in-situ* sampling design was focused on an inshore-offshore transect approximately perpendicular to the Sicilian coast, composed by 10 stations spaced about 12 NM, comparable to the Ross by deformation radius (Sorgente et al., 2011).

Hydrological Data

The long-term variability in the hydrological characteristics of the SC has been analyzed on the basis of vertical profiles of



potential temperature (θ° C), salinity (S) and dissolved oxygen (DO mg/l) obtained from the surface to the bottom by means of a Conductivity Temperature Depth (CTD-rosette system; Tab. 1). It consists of a SBE 911 plus probe and a General Oceanic's rosette, equipped with 24 Niskin bottles. Moreover, the Chlorophyll-a concentration (Chl-a µg/l), measured from the fluorescence probe, has been examined to characterize the productivity of the upper water column. The probes were calibrated before each oceanographic survey. The collected downcast data were quality-checked and processed in agreement with the Mediterranean and ocean database instructions (Brankart, 1994), using the Seasoft-Win32 software. The overall accuracies are within 0.001°C for temperature, 0.001 sm⁻¹ for conductivity, and 0.015% of full scale for pressure.

Temperature and Salinity Time Series

The interpretation of the θ , S, σ , DO profiles and of the θ_{-} S diagram carried out in each station and in all the years has allowed us to recognize the various main water masses present in the study area, i.e. the SW (0-100 m depth, essentially consisting of AW), of the sub-superficial IW (200-500 m depth, mostly consisting of LIW) and locally also the upper part of the DW (>500 m depth) (**Figure 2A; Table 1; Supplementary 1**). Specifically, the AW and LIW were identified through the

minimum and maximum of salinity that characterizes their core, respectively.

For the computation of the θ and S time series of the AW core we used, for each station and for each year, the average value of θ and S included in the layer between the minimum of salinity and 10m below it (Bonanno et al., 2014), while for the IW core we used the average value of θ and S in the layer between the maximum salinity and 100m below it (Gasparini et al., 2005). Finally, for the DW we used, for each station and for each year, the average value of θ and S included in the layer between 500m-bottom, identified by the presence of a strong vertical gradient of θ , S and DO, clearly visible during the bansic14 and bansic15 surveys (**Figure 2B**). In this context, we worked on a clear signal of water masses characteristics, minimizing as much as possible the effects related to the mixing of the various water masses.

Nutrient Data

Marine water samples were collected from the surface to the bottom by means of Niskin bottles (**Table 1**). In particular, a variable number of fixed depths has been considered (surface-25m-50m-75m-100m-150m-200m-300m-400m-500m-600m-700m-800m-900m-1000m-bottom). All materials used for water sampling were earlier conditioned with 10% HCl and rinsed 3 times with ultrapure water. Unfiltered samples were

Station	Longitude [°E]	Latitude [°N]	Bottom depth [m]	Bansic10 (25 June– 14 July 2010)	Bansic11 (8 July–26 July 2011)	Bansic12 (4 July–23 July 2012)	Bansic13 (26 June– 16 July 2013)	Bansic14 (22 July–9 August 2014)	Bansic15 (16 July–3 August 2015)	Bansic16 (30 June– 14 July 2016)	Bansic17 (13 June–29 June 2017)	Bansic18 (07-19 September 2018)	Bansic20 (16-24 September 2020)
122	13.8028	37.064	50	х	хо	XO	XO	XO	XO	хо	XO	XO	хо
284	13.67	36.892	725	x	хо	XO	XO	XO	хо	xo	XO	XO	xo
452	13.5415	36.718	350	хо	хо	XO	XO	XO	хо	xo	х	XO	хо
623	13.4108	36.545	1150	x	хо	XO	XO	XO	хо	xo	XO	XO	xo
790	13.2805	36.371	410	хо	хо	XO	XO	XO	хо	x	XO		
957	13.1512	36.199	720	x	хо	XO	XO	XO	хо	x	XO		
1059	13.0227	36.025	610	хо	хо	XO	XO	XO	хо	xo	хо		
1119	12.8937	35.851	130	x	хо	XO	XO	XO	хо	xo	XO		
1179	12.7647	35.679	280	хо	хо	XO	XO		хо	x	XO		
1239	12.636	35.506	55	x	хо	XO	XO		хо	x	XO		

TABLE 1 | Oceanographic surveys carried out in the sicily channel and relative sampling activities (x_CTD and o_nutrient analysis) carried out in the 2010-2020 period.



stored at -20° C. In the laboratory, the concentration of nitrate, silicate and phosphate (µmol/l) was measured by means of a Sial Autoanalyzer "QUAATRO" following classical methods (Grasshoff et al., 1999), adapted to an automated system. The limit of detection for the procedure was, 0.02, 0.01 and 0.006 µmol/l for nitrates, silicates and phosphates, respectively.

Nutrient Time Series

Inorganic nutrients time series were reconstructed on the basis of the physical characterization of the water masses, through which three main layers (i.e. surface waters, SW; intermediate waters, IW; deep waters, DW) were identified with the relative depth ranges: 0-100; 200-500; 500-bottom (**Figures 2**, **5**). Specifically, each layer was associated with a load of inorganic nutrients (nitrates and silicates) calculated as the average concentration (μ mol/l) detected in all the water samples contained within each layer and for each year (**Supplementary 2**).

Satellite Data

The satellite data were used in order to provide a description of the physical features occurring in the surface layers during the sampling periods. Therefore, mesoscale structures, such as currents, fronts and gyres, were observed by means of Absolute Dynamic Topography (ADT) (L4 gap-free monthly data; spatial resolution: 0.125x0.125 degree) and ADT-derived geostrophic velocity fields, produced by Copernicus Marine Environment Monitoring Service (CMEMS, http://marine.copernicus.eu/). Annual mean maps of ADT and geostrophic currents have been analysed in order to provide a description of the main surface circulation patterns occurred during the considered time series in the Central Mediterranean Sea. Furthermore, vorticity has been computed starting from the geostrophic velocities derived from satellite data for each grid point within the box [37.5°-39° N] and [17.5°-20°E], following the procedure described by Shabrang et al. (2016), more recently also applied by Notarstefano et al. (2019) and Mihanovic et al. (2021).

Statistical Analysis

The correlation between temperature and salinity patterns observed in the SC (i.e. positive/negative trends) and the circulation mode of the NIG (i.e. cyclonic/anticyclonic phase) was investigated through a cross-correlation analysis, considering a time lag ranging between 0 and 15 years and applying Cramer's V as a measure of association between the two nominal variables.

RESULTS

Temporal Trends of Hydrological Characteristics

Oceanographic surveys were carried out in different periods of the summer season (June-September, see **Table 1**). The average θ and S in the SW layer varied between 16.7°C and 19.3°C and between 37.4 and 37.6, respectively (**Figure 3**). This layer is characterized by a strong interannual and spatial variability (in terms of standard deviation), especially in 2012, and does not present a clear trend.

The IW layer is characterized by a lower spatial variability and a clear positive trend in terms of θ and S from 2010 to 2017 (d θ / dt ~0.09°C yr⁻¹ and dS/dt ~0.016 yr⁻¹), while a weak decrease is registered between 2018 and 2020 (d θ /dt ~-0.04°C yr⁻¹ and dS/dt ~-0.007 yr⁻¹). Our estimations are comparable with Schroeder et al. (2017), who reported a d θ /dt ~0.064°C yr⁻¹ and dS/dt ~0.014 yr⁻¹ in 2011-2016.

Finally, the θ and S time series recorded in the upper DW was characterized by a positive trend and by a lower variability, in which θ varied between 2010 and 2020 with an $d\theta/dt$ of 0.027° C yr⁻¹(**Figure 3**) while S varied between with an dS/dt of 0.005 yr^{-1} . The θ and S time series can be represented by two patterns, a positive one occurring from 2010 to 2016, with an d θ/dt of 0.05° C yr⁻¹ and an dS/dt of 0.01 yr^{-1} , followed by a slightly negative trend where the θ dropped to 14.096°C with an d θ/dt of -0.01° C yr⁻¹ while the S dropped to 38.835 with an dS/dt of -0.002 yr^{-1} (**Figure 3**).

Inorganic Nutrient Distribution Patterns

The nitrates, silicates and phosphates distribution patterns *vs* depth showed very low concentration values in SW (often below the instrumental detection limit for phosphate) most probably linked to their depletion by the phytoplankton for its



photosynthetic activity (Figure 4; Table 1; Supplementary 2). In the last decade the deep chlorophyll maximum (DCM) developed in the depth range 50-120 m (with peaks of maximum concentration around 70-80 m of depth), with the exception of July 2013, in which high fluorescence values (0.76 μ g/l) were measured at 39 m of depth (Figure 4). Under the SW and the DCM, nutricline, silicocline and phosphocline developed with different slopes and depth and mirrored the decrease in dissolved oxygen. Higher oxygen concentrations were recorded close the Sicilian coast, at about 50 m depth within the nutrient depleted layer (Figure 4). The maximum concentrations of nitrates, silicates and phosphates of 7.66 µmol/l (St. 790 at 400m depth), 9.55 µmol/l (St. 284 at 700m depth) and 0.35 µmol/l (St. 790 at 400m depth) were detected during the 2011-2012-2017 surveys, respectively (Figure 4), while the average concentration of nutrients, for each water mass, are reported in **Supplementary 2**. The vertical profiles of nitrates to phosphates, in the years, show low values in the SW respect to IW and DW, with the regression line characterized by R²>0.8 (Figure 4). The box plot of the N:P ratio, highlighted low values in the SW that increase to values >40 in the IW (with average value of 32), while in the DW the average value is 30 (Figure 4). These values are in agreement with the data reported for the SC by various authors (e.g. Ribera D'Alcalà et al., 2003; Schroeder et al., 2010; Placenti et al., 2013).

Temporal Trend of Biogeochemical Characteristics

The nitrate-silicates time series related to the SW highlighted a lower concentration values and variability over time compared to IW and DW (Figure 5). Nitrates showed a slightly negative trend in 2011-2016 and then it turned to be positive until 2020 (Figure 5). The silicates pattern was characterized by a more evident negative trend (2011-2016), in which the average concentration decreased from 0.93 to 0.38 µmol/l (-0.091 μ mol/l yr⁻¹), and then increased to 0.88 μ mol/l in 2020 (Figure 5). In the IW the nitrates and silicates highlighted similar concentration distribution patterns. Two trends can be distinguished, one negative (2011-2015) and one positive (2015-2018; Figure 5). In the first trend the average concentration of nitrates and silicates decreased by -0.61 and -0.54 µmol/l yr⁻¹, respectively. In the second trend, the average concentration of both nutrients increased by 0.47 μ mol/l yr⁻¹ (Figure 5). Average concentrations of nutrients dropped slightly in 2020, probably reflecting the start of a new cycle.

The DW was characterized by distribution patterns of average concentrations of nitrates and silicates similar to the IW, in which it was possible to outline two general trends: the first negative (2011-2015) and the second slightly positive (2015-2017/2018) (**Figure 5**). Finally, the average concentrations of both nutrients dropped slightly from 2017-2018 to 2020 (**Figure 5**).



Although with higher variability, similar patterns emerged considering the chlorophyll-a concentration occurring in the surface layer (0-120m) (**Figure 5**). In particular, a significant positive Pearson correlation coefficient (r) has been computed between the sum of the scaled nutrients concentration (nitrates, silicates, phosphates) in the IW and the chlorophyll-a concentration in the upper layer (r= 0.67; p<0.05).

DISCUSSION AND CONCLUSION

While the surface temperature is able to provide the almost instantaneous signature of interactions with the atmosphere, which is by its nature subjected to great variability, the analysis of the variability of the heat and salt content in the deeper water masses provided a climate index more suitable for monitoring any changes over long periods. For this reason, we have integrated the intermediate and deep layer dataset with the previous ones carried out by Bonanno et al., 2014 and Ben Ismail et al., 2014 (**Figure 6**). Regarding the IW layer, time series presented in this study are in agreement with comparable time series collected in the SC by Gasparini et al., 2005; Gačić et al., 2013; Ben Ismail et al., 2014; Bonanno et al., 2014 and Schroeder et al., 2017. Specifically, it is thus possible to highlight a general increasing trend and the presence of "cyclic patterns" in temperature and salinity, that could be associated with the alternation of different circulation modes (cyclonic and anticyclonic) of the NIG in addition to IW formation processes. In particular, we infer an average annual increase of dT/dt ~0.047°C yr⁻¹ and dS/dt ~0.01 yr⁻¹ from the 1998-2007 (Figure 6), comparable to those estimated by Gasparini et al. (2005) and Schroeder et al. (2017). Such a trend of T and S could be related to the anticyclonic phase of the NIG estimated from 1988 to 1997 (mean ADT available from 1993 to 1997, Figures 7A, E), according to Bonanno et al., 2014. The anticyclonic circulation inhibits the AW advection to the southern Levantine basin, favouring the production of saltier and warmer IW, whose effects were observed in the SC with a variable time lag that deserves further studies and insights. The period 1998-2007 is followed by an abrupt reversal trend up to 2010, characterized by a dT/dt of -0.12°C yr⁻¹ and dS/dt of -0.01 yr⁻¹ (Figure 6). These trends, in agreement with Gačić et al., 2013; Ben Ismail et al., 2014; Bonanno et al., 2014; Schroeder et al., 2017, could be linked to the previous cyclonic phase of the NIG (1998-2005, Figures 7B, E). It favoured the strengthening of the MIJ and thus the AW advection to the southern Levantine basin, leading to an increasing of the water masses dilution in the EMS, according to Schroeder et al., 2017. Approximately, a new







indicated as green and blue dots, respectively. Potential temperature and salinity time series from this study are indicated as red dots. A cubic regression spline computed through a GAM model and the relative confidence interval has been added in gray with the aim at evidencing temporal trends. Black arrows indicate the average annual increments of hydrological parameters computed for 1998-2009 by Bonanno et al. (2014) and for 2010-2020 from data collected in this study. The position of the dots on the time axis takes into account the sampling month.

salty/warm phase occurs from 2011 until 2017 (Figure 6), probably associated to the previous anticyclonic phase of the NIG (2006-2010, Figure 7C). Compared to the first average annual increase in θ and S, attributable to the anticyclonic phase 1993-1997, this increasing trend shows considerably higher rates of $d\theta/dt$ and dS/dt, despite being related to a shorter and less defined anticyclonic circulation. Indeed, some authors identified the 1993-1997 phase as "fully anticyclonic" due to the absence or weak activity of the MIJ. Differently, during the subsequent anticyclonic phase (2006-2010), the MIJ occurs with an intense, non-negligible, zonal activity from the SC to the Levantine basin, prompting authors to distinguish this period as an "anticyclonic-zonal" phase (Bessières et al., 2013). Therefore, our considerably higher rates of increase in θ and S can be only partially associated with the anticyclonic-zonal phase of the NIG, from which a lower rate of increase would be expected. A further possible explanation could be linked to the increasing of the drying process (E-P), affecting the surface waters from which LIW and CIW originate, in agreement with Schroeder et al. (2017).

The last period of the time series (2018-2020, Figure 6) showed a new decreasing trend significantly lower than the

previous one (i.e. 2008-2010). This last reversal trend followed the cyclonic phase occurred in 2011-2016 (Figures 7D, E). The comparison of the ADT averages observed during the two cyclonic phases (Figures 7B, D) allowed to evidence a significant difference in term of intensity and areal extension of the NIG. In the first phase the NIG extends down to 35°N while in the second phase is confined at northern latitudes, higher than 36.5°N, probably due to the presence of an anticyclonic structure in the centre of the IS (Cardin et al., 2015; Placenti et al., 2018). This structure has weakened the AW flux toward Levantine Basin (Cardin et al., 2015), limiting the influence of colder and fresher AW toward the area where the formation of the IW take place. This interpretation is supported by recent studies that found a premature inversion of the NIG from cyclonic to anticyclonic, related to the extremely strong winter 2012 in the Adriatic (Gačić et al., 2014) leading to a strong weakening of the AW flux toward Levantine Basin between mid-2012 and the first months of 2013 (Menna et al., 2019). This phenomenon probably produced, between 2012 and 2013, warmer and saltier IW in the EMS which could have modulated the decreasing rate of θ and S in the SC.





The correlation between the NIG circulation mode and the temperature and salinity trends observed in the SC was investigated through a cross-correlation analysis that show a significant correlation for time lag of 6 (Cramer's V = 0.456, p < 0.05) and 7 years (Cramer's V = 0.497, p < 0.05), highlighting an association between cyclonic phase-negative trends and between anticyclonic phase-positive trends. However, we recognized a temporal variability between the reversal of the circulation mode and the trend inversion that suggest the

presence of unadressed additional mechanisms that tune the onset of the signals and encourage the need of further studies.

Moreover, the time series of θ and S of the DW in 2010-2020 has been investigated and showed similar trends to the IW, but characterized by lower increments (**Figure 3**). However, it is important to note that most of the data collected in this study regarding the DW are referred to the upper part of this water mass, due to the limited depths that characterize the SC. Regarding this water mass, integrating the θ and S data discussed in Bonanno et al. (2014) and Ben Ismail et al. (2014) with our time series, it is possible to detect a general increase in the last twenty years of about 0.4°C of θ and 0.1 of S, respectively (Figure 8). However, the time series showed two strong break points in 2006 and 2009 characterized by an abrupt decrease of θ and S that were also discussed by Ben Ismail et al. (2014) regarding the 2006, and by Bonanno et al. (2014) regarding both years. In addition, these authors found a simultaneous increase of density (σ) in the DW, associating these findings to the presence of tEMDW in the SC. It is confirmed by our data also in 2010 (not shown), while in the following years (2011-2017) a new warm and salty phase seems to affect the deeper waters of the SC (Figures 6 and 8). We also hypothesize that these trends concerning the deeper layers are a direct response to the climate change, in particular in terms of net evaporation over to the eastern basin, i.e. where the deeper water is formed (Schroeder et al., 2017).

The coupling of the nitrates and silicates time series (2010-2020) with the salinity in the deeper waters of the SC showed anti-phase trends (**Figure 5**). These trends have been observed in IW both in the EMS (Ozer et al., 2017) and in the AdS (Borzelli et al., 2009; Civitarese et al., 2010). In agreement with Ozer et al. (2017), we think that a possible explanation could be related to the surface circulation dynamic of the NIG.

Specifically, during the anticyclonic phase (2006-2010, **Figure 7C**) the influx of AW, considered the main external source of P and N to the Mediterranean system (Powley et al., 2017), towards the Levantine Basin was limited, producing saltier and poorer nutrient IW. Conversely, the slight decrease in salinity and increase in nutrients observed between 2017 and 2020 (**Figure 5**) could be linked to the previous cyclonic phase of the NIG (2011-2016, **Figure 7D**).

In addition, the interannual fluctuations affecting the nutrient concentration has been compared to the variability of the Chl-a concentration, which is considered a good proxy of the phytoplankton biomass and provides useful indications on the productivity of the upper layer of the water column (e.g. Falkowski et al., 2004). Interestingly, our findings show similar trends among these time series, especially taking into account the nitrates and silicates concentration of the deeper layers. Indeed, starting from 2010, these time series were characterized by variable fluctuations and reached a simultaneous minimum peak in 2015, then followed by an increasing trend until the 2020. These observations suggest that vertical oceanographic structures, such as upwelling processes identified along the Sicilian coast (Lermusiaux and Robinson, 2001; Bignami et al., 2008; Patti et al., 2010; Torri et al., 2018), could play a significant role in the diffusion of nutrients from the lower layers, making them available for the photosynthetic activity





with a cascading effect on the marine organisms that in the Central Mediterranean Sea found a suitable habitat for feeding and reproduction (e.g. Bonomo et al., 2018; Patti et al., 2020; Russo et al., 2021). Indeed, it could also be noted that the SC is a place of strong diffusion and dissipation that may favor such vertical transport (Ferron et al., 2017; Vladoiu et al., 2018). However, discordant findings regarding this relationship emerged between our study areas and the Levantine basin, in which an opposite trend has been evidenced between the nutrient concentration of the IW and the Chl-a concentration (Ozer et al., 2017), suggesting the need of further studies on a wider scale. In this context, the long-time series in the Strait of Gibraltar and Sicily, which represent key points of the entire Mediterranean thermohaline circulation, are of fundamental importance for climate studies. It is necessary to continue maintaining long-term observational points to improve our understanding of the physical mechanisms that drive climate variability and to discriminate the effects related to natural variability and the anthropogenic effect. Similarly, in these key areas, the acquisition of nutrients high-quality data on a multiannual scale are essential for understanding the relationships between oceanographic, biogeochemical and biological processes.

DATA AVAILABILITY STATEMENT

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

AUTHOR CONTRIBUTIONS

FPI wrote the manuscript and analyzed the dataset. MT wrote the manuscript and prepared the figures. VT, LG participated to

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the fieldwork and laboratory analyses. BP, AC and GT coordinated the field work and supervised the writing of the text. RS and FPe helped with some specific aspects of the manuscript and to review the manuscript. All authors contributed to the article and approved the submitted version.

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SUPPLEMENTARY MATERIAL

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