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Oxygen dynamics in the Black Sea as seen by Argo profiling floats

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Abstract

Observations collected in the Black Sea from May 2010 until December 2011 from two Argo floats with oxygen sensors demonstrated the potential of the applied technique to deliver high-quality oxygen data in this oxic/anoxic environment where the oxygen concentration varies from the level of saturation to zero. It was demonstrated that the dynamics of the oxic-anoxic interface was dominated by vigorous mesoscale processes displacing locally anoxic waters up to about 70 m below the sea surface. Alternatively, oxygenation (ventilation) in the coastal zone penetrated down to about 150-200 m. The range of mesoscale variability, which appeared to reach half of the range of climatic trend during the last 50 years, helped to objectively assess the validity of interpretation of historical data. It was proved that the shift of the suboxic zone from isopycnal depth σ_t=16.5 to σ_t=15.5 during 1960-2010, interrupted by its deepening between 1990-2000 was greater than the possible error limit caused by insufficient sampling of mesoscale variability. Furthermore, profiling floats shed a new light into the seasonal variability of the subsurface oxygen maximum. It was also demonstrated that the assumption of isopycnal alignment of oxygen was coarsely applicable to the suboxic layer both in the coastal and interior part of the Black Sea where the isopycnal mixing revealed large temporal and spatial variability. Therefore deeper understanding of the dynamics of suboxic zone necessitated continuous basin-wide sampling.

1. Introduction

The oxic/suboxic/anoxic interface in the Black Sea is an important location for biogeochemical studies. Understanding its temporal and spatial variability is essential for understanding the processes that control its dynamics. Anoxic basins like the Black Sea (Skopintsev, 1975; Murray et al., 1989; Sorokin, 1982; Jørgensen et al., 1991, Murray et al., 1995) provide not only excellent laboratories to study fundamental processes associated with the long-term change of biogeochemistry on Earth, but also manageable systems to address the quality of sampling and develop new observational strategies. The Black Sea, which is the world's largest anoxic basin, is a deep ocean basin (∼2000m) connected to the Mediterranean by the narrow Bosporus Strait, Marmara Sea and Dardanelles. Because of the narrow and shallow opening in the straits, the two-way exchange between the Black Sea and the Mediterranean is small. The relatively large river runoff results in lower values of surface salinity (about $S = 18$) compared to the deep inflowing Mediterranean water (about $S = 36$). The pycnocline lies at about 150 m in the central Black Sea acting as a barrier to the winter convection. The cold intermediate layer (CIL) is a permanent cold layer at 50-100 m acting as a near-surface thermal reservoir, similar to the North Atlantic Subtropical Mode Water, which is renewed due to vertical mixing during cold winters (Stanev et al., 2003; Gregg and Yakushev, 2005). After the Mediterranean water exits the Bosporus Straits, it follows across the continental shelf of the Black Sea where it mixes with the overlying cold intermediate water (Murray et al., 1991). When this well oxygenated water with high temperature and salinity reaches the shelf break it is injected locally into the pycnocline (Konovalov et al., 2003). Due to the very stable stratification, the ventilation of the Black Sea is slow (Özsoy et al., 1993; Stanev et al., 2004) so that oxygen is totally consumed in the deep water by respiration of sinking organic matter (Murray and Yakushev, 2006). As a result, the deep water below the pycnocline is dominated by sulfate reduction. The oxic and sulfidic waters are separated by a layer between the isopycnal depths σ_t= 15.40 and 16.20 known as the suboxic zone (Murray et al., 2005). This zone is defined by Murray et al. (1989; 1995) as the region between where oxygen decreases to near zero ($O2 \leq 10 \mu M$) and where sulfide first appears.

Over the past few decades the ecological state of the Black Sea has been seriously perturbed by climatic change and land use including the damming of rivers (Humborg et al., 1997; Gregoire et al., 2008). Accordingly, hypoxic and anoxic conditions increased (Konovalov and Murray, 2001; Oguz et al., 2006), further deteriorating the Black Sea marine ecosystem as predicted for the aquatic stems world wide (Keeling et al., 2010).

In order to accurately decipher the long-term change in the hydrochemistry, short-term fluctuations must be well understood (Murray et al., 1989; Murray, 1991; Kempe et al., 1990; Turgul et al., 1992). Therefore a solid knowledge of the basin and sub-basin scale dynamics is needed, with particular regard to the temporal and spatial variability of oxic and anoxic conditions (Glazer et al., 2006).

In the present paper the first observations carried out in the Black Sea with profiling floats equipped with oxygen sensors are presented focussing on their potential to deliver high-quality oxygen data. Objectively evaluated uncertainties of the oxygen state estimates give more quality to the assessment of ecosystem health (Johnson et al., 2009) and could be used to develop improved monitoring of oxygen. The specific scientific aim of the present study was to: (1) focus on the mesoscale oxygen dynamics in a typical oxic/suboxic/anoxic basin; and (2) revise and update interpretations of historical observations.

2. Observations and Methods

In total about 120 thousand quality checked oxygen observations were taken during 1910-1999, most of them were in the upper layer (see the MEDiterranean ACCess (MEDACC) system for exploration and visualization of marine cast data, http://isramar.ocean.org.il/isramar2009/medacc/). The number of observations at 200 m was about 10 times smaller than at sea surface. The first high quality CTD data were collected in 1988 (Murray et al., 1991) and used to describe the hydrography and circulation of the whole water column. Recent observations with Argo floats equipped with oxygen sensors provide an efficient tool to monitor the upper layer hydrochemistry (Johnson et al., 2009; Gruber et al., 2009). Because the Black Sea is a deep basin, the use of Argo floats is an optimal solution not only for the physical variables (Korotaev et al., 2006), but also for oxygen. Profiling floats are autonomous devices drifting at fixed depths following oceanic currents. They can be programmed to change their buoyancy by modifying the total volume of the device, which enables vertical displacements within the water column. Presently there are nearly 3,000 profiling Argo floats, of which less than 100 have been equipped with oxygen sensors (Körtzinger et al., 2004).

During the first leg of R/V Maria S. Merian Cruise Nr. MSM 15 (07. 04. 2010 29. 07. 2010) two Navigating European Marine Observer (NEMO) profiling floats manufactured by Optimare Sensorsysteme AG Bremerhaven, Germany were deployed in the northern

Black Sea (Fig. 1a). They measured temperature, salinity and oxygen concentration along vertical profiles in regular intervals of five days. Data transmission used IRIDIUM satellite system by Short Burst Data (SBD) packages. NEMO-145 measured with vertical discretization of 2 m providing altogether maximum 255 data in the upper 500 m. NEMO-0144 measured 116 data in the same depth interval, however with a coarser resolution in the upper and deeper layer (the coarsest resolution was 20 m below 240 m). Deployment times and coordinates were correspondingly 7.5.2010, 8:17, $44^0$10.00'$\times 32^0$ 30.01' and 7.5.2010, 9:54, $44^0$0.02'$\times 32^0$4.92'. NEMO-0144 ended operations on 28.12.2011, NEMO-0144 on 27.11.2012.

The sensor for temperature and salinity was CTD SBE 41, the one for oxygen was Anderaa Oxygen Optode 3830. Oxygen sensors show little or no drift and high accuracy (Johnson et al., 2009; Riser and Johnson, 2008). In the Black Sea there is a "natural calibration" every time when the float produces a new profile because there is a "solid zero" at depth. Analysis of data in the anoxic layers never showed values higher than 1 μM, which can roughly be taken as an error-estimate for the analyses presented in this paper. Furthermore, comparisons with historical observations (see next section) demonstrated that the sensors used provide credible results.

The initial positions of two floats were very close in space however their trajectories departed rapidly one from another after the deployment. The first float (NEMO-0144) entered the central basin (deep ocean), the second one (NEMO-0145) followed the upper continental slope. The oxygen observations collected by these floats amounted to about 1/5 of the total number of available oxygen data today.

3. Historical and profiling float data

3.1. Validity of the concept of isopycnal allignement

The comparison between profiling float data and historical observations demonstrates the consistence of the new measurements. Furthermore it enables to objectively decipher oxic conditions and changes in the Black Sea hydrochemistry in the area of suboxic zone. In the following the advantages of the two data sets (long-term sampling in the historical data and continuous sampling in the profiling float data) is put together in a complementary manner.

Oxygen plotted against density anomaly (Fig. 1b, c) revealed a general similarity between the data of two floats: (1) large variations in the upper layers down to σ_t=14 associated with the dynamics of the seasonal thermocline and biogeochemical processes; (2) an overall linear relationship between oxygen and density in the upper halocline (between σ_t 14 and 15), and (3) a transition to anoxic conditions below σ_t =15. The linear relationship between oxygen and density in the upper layers resembled similar relationships for other tracers (Shaffer, 1986; Stanev et al., 2004). This specificity of the Black Sea stratification motivated researchers to use density (salinity) coordinates to describe the overall distribution of properties because this presentation reduced data-scatter seen in depth coordinates, and rendered analyses quasi-independent from the specific location. However the mesoscale dynamics and diapycnal mixing, along with the biogeochemical activity related to the production, transport and remineralization of organic matter adds a considerable complexity to the assumption of density-oxygen alignment, in particular below the linear part of the profiles' data in Fig. 1b, c. The observed in the Argo-data spread of oxygen defined here as the rms difference between all observations at particular isopycnic surface and the respective mean value approaches the mean value at σ_t=16, that is in the suboxic zone (see the insets in Fig. 1b, c). It is noteworty that the mean and rms at σ_t=16 are above the error level ($\sim 1\mu$M), which justifies the conclusion that the values of the signal (mean concentration) and "noise" (rms variations) were resolved by the sensors. Because the level of signal is comparable to the one of noise in the area of suboxic zone (see also the scatter around $\sigma_t = 16$ in Fig. 1b, c), the assumption of density alignment is not valid basin-wide, unlike to the case between σ_t 14 and 15. Therefore extending the interpretations of local observations in the suboxic zone basinwide should be made carefully.

3.2. Recent trends

The results presented in the previous section motivated comparison between the present continuous observations and the highly cited literature data (see the legend in Fig. 1 for the inventory of the used surveys) for a 50-years period. Only the observations in the deep part of the Black Sea were used in the comparison in order to avoid the large variability in the coastal ocean, which could mask climatic signals because of insufficient sampling (aliasing problem). The overall shapes of the linear part of profiles did not change substantially during the last 50 years (Fig. 1b). However a displacement of concentrations towards lower density (almost parallel shifts between σ_t=15.5 and σ_t=14.5) revealed the long-term shoaling of oxygen penetration (see also Fig. 2a) during 1980-2010, which was interrupted for 10 years, from 1990 to 2000, by a pronounced deepening of oxic waters, and once more (noticeable in the upper pycnocline) around 2003. The trends described are consistent with the earlier analyses (Konovalov and Murray, 2001). The caveat is that the events associated with the short-time increase in oxygen concentration could result in misinterpretation of the long-term climatic signal (see Fig. 2b). Noteworthy is the sporadic deepening of the isoline 10 μM. During 2010-2011 this isoline several times reached σ_t =16, which was the normal position of the suboxic zone in 1970-1980 (compare Fig. 2b with Fig. 2a). Obviously, the strong intra-annual oxygen variability ($\sim 2\mu$M at σ_t 15.5-16), which is comparable with the 20 years trend during 1970-1990 of $\sim$5 μM, necessitates more careful interpretation of long-term changes. Nevertheless, displacement of the suboxic layer towards lower density during the last 50 years, which is the major signal in the Black Sea hydrochemistry, seems to have been relatively well resolved in historical data.

3.3. Mesoscale dynamics

The temporal evolution of vertical profiles of oxygen, temperature and salinity (Fig. 3) demonstrated how powerful continuous observations are for the understanding of thermohaline and oxygen dynamics in the coastal and central basin areas. Subsurface oxygen maxima in summer reveal the role of the enhanced photosynthetic productivity in the upper mixed layer. Similar features were observed in other ocean basins (Riser and Johnson, 2008). The subsurface maximum persisted until October-November and vanished with the disappearance of the seasonal thermocline (Fig. 3a, b).

The oxygenated layer in the upper ocean was about two times thinner in the central basin than in the coastal zone, and the temporal variations of its thickness were very small (about 20 m). In contrast, the depth of the oxic-anoxic water interface around the continental slope represented by the isoline 5μM (red isolines in Fig. 3a, b) underwent changes of more than 75 m in only several weeks travel time. The difference between the coastal and central basin waters was easily noticeable in the thickness of the oxygenated layer confined between isolines 50 and 5 μM (h_5^{50}). This thickness was ~20 m in the slope area and ~10 m in the interior Black Sea. While the oscillations of h_5^{50} seen by NEMO-144 (central basin) seldom exceeded 15 m, the ones measured by NEMO-145 (coastal ocean) could reach 40 m, and even larger values (50-60 m) in the proximity of the Bosporus Strait.

A number of strong upward bursts of low oxygen waters reaching 50 m (75 m in the coastal zone) were observed, manifesting the importance of the mesoscale processes for the depletion of oxygen. Oxigenation/ventilation of the pycnocline also showed pronounced mesoscale characteristics. The correlation with the dynamics of halocline (compare with Fig. 3 e, f) demonstrated that in most cases mesoscale eddies contributed largely to the variations of oxygen (the increase of oxygen occured at the time of decrease of salinity). A similar role of mesoscale dynamics for temperature was revealed in earlier studies (Stanev and Staneva, 2001). The white-dashed lines display the concentration of oxygen at σ_t =15.8 (Fig. 3a) and σ_t =16 (Fig. 3b). While the ventilation events were clearly seen both in z and σ_t coordinates, their relative maxima were very different illustrating that diapycnal mixing was quite complex. For some events (e. g. the one in November 2011 seen by NEMO-0144) there was almost no "counterpart-event" in the halocline depth.

Dark blue colour and isolines in Fig. 3c, d display the formation and evolution of CIL. Winter cooling pumped cold surface water into deeper layers, but convection was limited to the depth of the pycnocline. This layer was refilled every year in February-March.

The variations in the depth of its lower boundary correlated with the oscillations of the depth of the pycnocline, which was very pronounced in the coastal zone. Its thickness in the central basin was smaller than in the coastal zone reflecting the impact of upwelling and downwelling, respectively. Like in the case with oxygen the mesoscale variability in the central basin was very low. Temperature in the core of CIL was in most of the cases higher than 8^oC, which did not to support the usually accepted definition of CIL as a permanent layer at 50-100 m with temperatures lower than 8^oC (Blatov et al., 1984). In order to exclude possible problems in the sensors of NEMO-144 and NEMO-145 all available profiling floats data in the Black Sea from 14/03/2005 (14 floats all together) were checked. From 1164 profiles in total, 946 profiles showed intermediate minimum, in the remaining 218 ones the minimum was at the surface (the usual winter case). In only 241 profiles (20.70 percent of the total) the CIL was colder than 8^oC. This explains why the isoline 8.35^oC was used in Fig. 3c, d to visualise the CIL and suggests revisiting the long-term changes of Black Sea heat content or the accepted definition for CIL.

4. Conclusions

First observations carried out in the Black Sea with Argo floats equipped with oxygen sensors demonstrated clearly the potential of this new observational platform to deliver high-quality data in a basin where the oxygen dynamics couples with the dynamics of deep anoxic waters. Application of the new observations to study the dynamics of oxic-anoxic interface was the major novelty of this study. It was demonstrated that mesoscale processes contributed largely to the dynamics of suboxic zone bringing anoxic waters up to about 50 m or deepening of the pycnocline down to 150-200 m. As a consequence of the strong mesoscale activity isopycnal mixing increased considerably. Furthermore, it was demonstrated that concepts assuming isopycnal alignment of properties in the suboxic layer were coarsely applicable to both coastal and interior part of the Black Sea.

Profiling floats provide also a very useful tool to observe the seasonal variability of the subsurface oxygen maximum and to establish the rate of mesoscale variability of oxygen. The new observations give more confidence to the interpretation of historical data, in particular concerning long-term changes. It was demonstrated that the shift in the upper boundary of suboxic zone from isopycnal depth σ_t=16.5 to σ_t=15.5 observed in the last 50 years exceeded the mesoscale "noise", which gives more confidence of some earlier conclusions about long-term changes in the Black Sea hydrochemistry.

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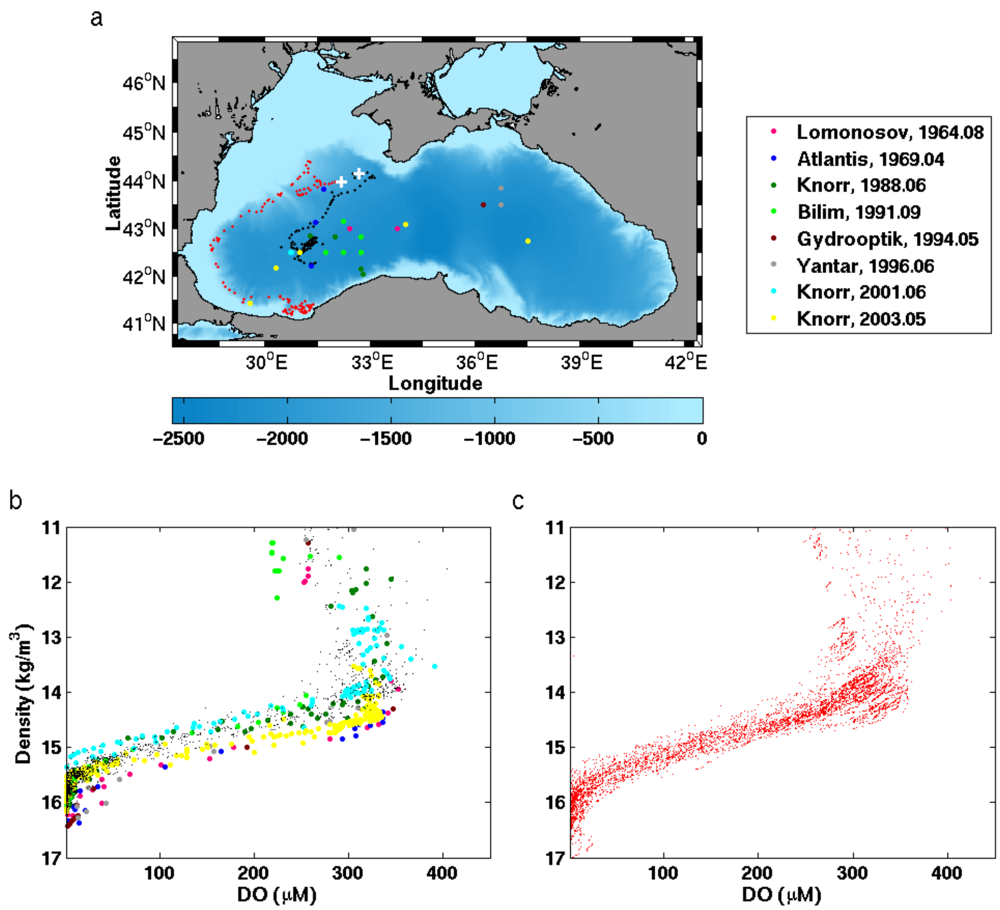
Figure Caption

Figure 1. (a) Black Sea topography. The colour bar indicates ocean depths in meters. The locations of surfacing of NEMO floats (NEMO-0145 following the coast and NEMO-0144 remaining in the central basin), once per five days, are plotted with small red and black dots, correspondingly. The first profile of each float is displayed by + symbol. Positions of historical observations discussed in the text are plotted with symbols (see legend where vessel name, year and date are also given). Oxygen versus density anomaly as seen in the data from NEMO-0144 (b) and NEMO-0145 (c). NEMO-0144 data have been plotted after the float has reached the deep sea. Fewer data in the case of NEMO-144 is due to the coarser vertical sampling. Historical observations in the central basin (symbols correspond to the ones indicating locations in Fig. 1a) are compared with the data from NEMO-0144. The insets in (b) and (c) show the ratio between the mesoscale noise (rms) and signal (mean value) between σ_t=15 and σ_t=16.

Figure 2. (a) Time versus isopycnal depth plot of historical data presented in Fig. 1a with the addition of two Argo profiles in September 2010 and September 2011. Arrows indicate the time of observation. (b) The same for NEMO-0144 in the central basin. In order to make the evolution of oxygen in the pycnocline clearer, surface data, which will be addressed further in text, have been excluded. Isolines 50, 10 and 5 μM are plotted with white, red and yellow lines, correspondingly. The two straight lines illustrate possibilities of misinterpretations of trends in the 5 μM isoline resulting from insufficient sampling (four observations during different times).

Figure 3. Temporal evolution of oxygen (in μM), temperature (in ^0C) and salinity (in practical salinity units) as observed by NEMO-0144 (left) and NEMO-0145 (right). Upper two panels (a and b) illustrate the evolution of subsurface oxygen maximum and the mesoscale variability of the interface between oxic and anoxic waters. The white and red isolines identify oxygen concentrations of 50 (5) μM, respectively. The dashed white lines display the oxygen concentration at σ_t=15.8 (a) and 16 (b); the labels are on the right y-axis. The dashed line in (b) is not plotted for the whole period because in the proximity of the Bosporus Straits oxygen dynamics is not representative for the rest of the basin. The plots in the middle (c and d) illustrate the formation and evolution of the CIL bounded by the plotted with white (red) isothermals of 8 (8.35) ^{0}C, respectively. The bottom two panels (e and f) display the salinity stratification, with halocline bounded by of 18.3 (red) and 19.9 (blue) isolines, respectively. Note that in the basin interior (NEMO-0144) the temporal evolution of the depth of isopycnals is very small. White vertical strips illustrate missing data due either to malfunction of sensors or to reaching bottom.



a
46°N
45°N
44°N
43°N
42°N
41°N
Latitude
30°E
33°E
36°E
39°E
42°E
Longitude
-2500
-2000
-1500
-1000
-500
0
Lomonosov, 1964.08
Atlantis, 1969.04
Knorr, 1988.06
Bilim, 1991.09
Gydrooptik, 1994.05
Yantar, 1996.06
Knorr, 2001.06
Knorr, 2003.05
b
Density (kg/m³)
11
12
13
14
15
16
17
100
200
300
400
DO (μM)
c
11
12
13
14
15
16
17
100
200
300
400
DO (μM)

Fig. 1.

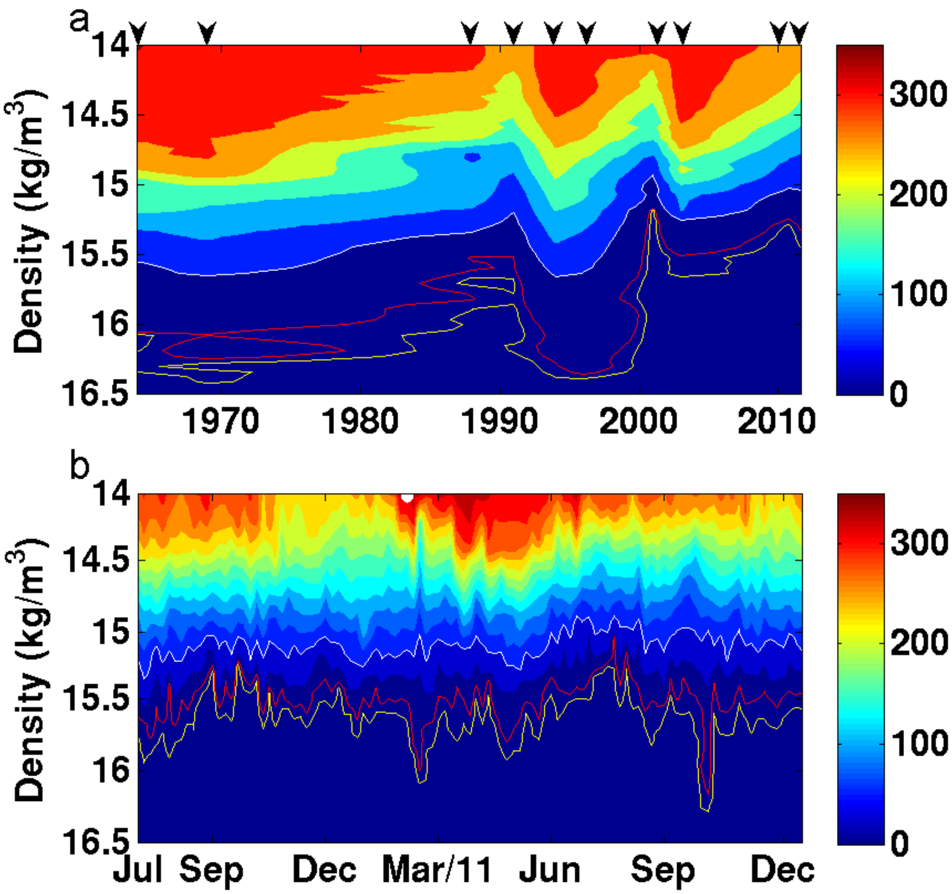
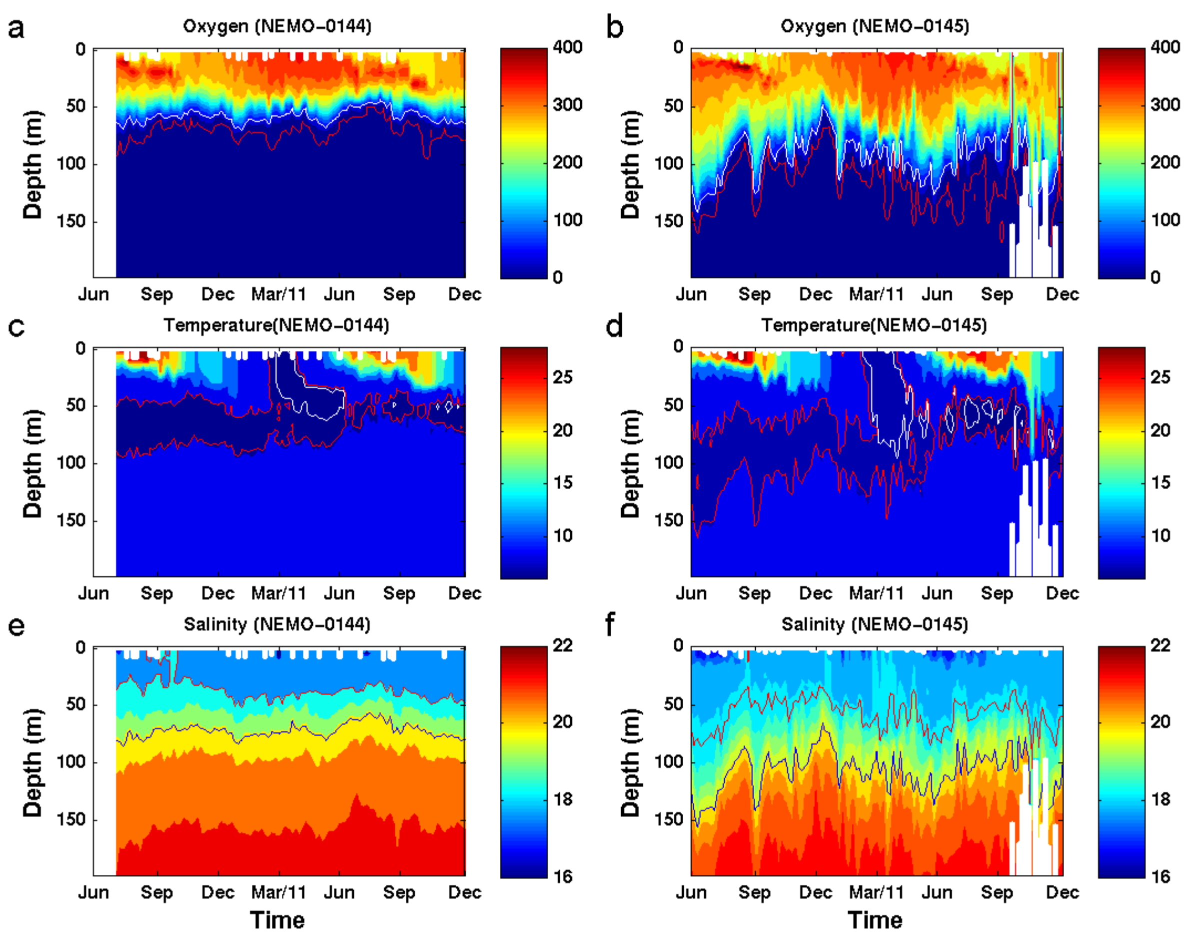

a
b
Density (kg/m3)
14
14.5
15
15.5
16
16.5
1970
1980
1990
2000
2010
Jul
Sep
Dec
Mar/11
Jun
Sep
Dec
0
100
200
300

Fig. 2.



a
Oxygen (NEMO−0144)
b
Oxygen (NEMO−0145)
c
Temperature(NEMO−0144)
d
Temperature(NEMO−0145)
e
Salinity (NEMO−0144)
f
Salinity (NEMO−0145)
Depth (m)
Jun
Sep
Dec
Mar/11
Time

Fig. 3.