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Seasonal and interannual variability of dissolved oxygen around the Balearic Islands from hydrographic data

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Abstract

Oceanographic data obtained between 2001 and 2011 by the Spanish Institute of Oceanography (IEO, Spain) have been used to characterise the spatial distribution and the temporal variability of the dissolved oxygen around the Balearic Islands (Mediterranean Sea). The study area includes most of the Western Mediterranean Sea, from the Alboran Sea to Cape Creus, at the border between France and Spain. Dissolved Oxygen (DO) at the water surface is found to be in a state of equilibrium exchange with the atmosphere. In the spring and summer a subsurface oxygen supersaturation is observed due to the biological activity, above the subsurface fluorescence maximum. Minimum observed values of dissolved oxygen are related to the Levantine Intermediate Waters (LIW). An unusual minimum of dissolved oxygen concentrations were also recorded in the Alboran Sea Oxygen Minimum Zone. The Western Mediterranean Deep Waters (WMDW) and the Western Intermediate Waters (WIW) show higher values of dissolved oxygen than the Levantine Intermediate Waters due to their more recent formation. Using

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these dissolved oxygen concentrations it is possible to show that the Western Intermediate Waters move southwards across the Ibiza Channel and the deep water circulates around the Balearic Islands. It has also been possible to characterise the seasonal evolution of the different water masses and their dissolved oxygen content in a station in the Algerian sub-basin.

Keywords: Ocean circulation, dissolved oxygen, water masses, Western Mediterranean Sea, Balearic Sea

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1. Introduction

The Balearic Islands are the natural limit present between two sub-basins of the Western Mediterranean Sea, viz., the Algerian and Balearic sub-basins (Fig. 1). The Algerian sub-basin receives fresh surface water from the Atlantic Ocean (Atlantic Water, AW), and its circulation is mainly driven by density gradients. The Balearic sub-basin contains the colder and saltier AW that has remained for a longer time in the Mediterranean (resident AW), and its circulation is affected by atmospheric forcing (Hopkins, 1978). The Mallorca and Ibiza channels play an important role in the regional circulation of the water masses in the area. Their topography controls the exchanges between the two sub-basins (Pinot et al., 2002). Consequently, significant differences are visible between the general hydrodynamic conditions that affect the northern and the southern regions of the Balearic Islands. The confluence of the fresher and resident surface AW around the Balearic Islands triggers ocean fronts that affect the dynamics (López-García et al., 1994; Balbín et al., 2013).

Two intermediate waters are present surrounding the Balearic Islands, viz., the Levantine Intermediate Water (LIW) and the Western Intermediate Water (WIW). The LIW, formed in the Eastern Mediterranean Sea, is characterised by an absolute maximum of salinity, a relative maximum of temperature and an absolute minimum of dissolved oxygen (DO). The WIW, on the other hand, is formed seasonally during the winter convection processes in the Gulf of Lions over the continental shelf extending from the Ligurian Sea to the Ebro Delta (Vargas-Yáñez et al., 2012). The WIW lies above the LIW, and varies in thickness from tens to a few hundred metres. It is characterised by an absolute minimum of temperature and shows relative high values of DO. Just below the WIW and LIW lies the Western Mediterranean Deep Water (WMDW), formed during the deep winter convection events in the Gulf of Lions and the Ligurian Sea (MEDOC-Group, 1970). Table 1 shows the salinity, S and potential temperature, θ, that characterise the different water masses and their values in the area, after López-Jurado et al. (2008); Table 2 shows the spatially averaged water properties in the Gulf of Lions and the Alboran Sea after Manca et al. (2004). The intermediate and deep water masses reach the Balearic channels after circulating along the continental slope of the north western Mediterranean. The WIW is dragged by the Northern Current (NC) into the Gulf of Valencia and the Ibiza channel towards the end of the winter and until the beginning of the spring, although it is not found in the Balearic channels every year (López-Jurado et al., 2008).

The vertical and horizontal distributions of the DO in the oceans reflect a balance between the exchange across the air-sea interface with the atmosphere, its involvement in the biological and chemical processes and its physical transport. Oxygen solubility is strongly temperature dependent and decreases at higher temperatures. Within the mixed layer, the DO very closely approaches the temperature-dependent saturation concentration. The oxygen solubility lowest concentrations are reached during late summer, while the highest are seen in late winter (Najjar and Keeling, 1997).

At the sub-surface level, the atmospheric supply is supplemented by the oxygen released during the photosynthetic processes occurring in the photic zone (Chester, 2000). As photosynthesis can produce a DO supersaturation, a shallow DO maximum has been reported in some oligotrophic marine regions like the Mediterranean Sea (e.g. Deya-Serra, 1978; Manca et al., 2004). On the contrary, the sub-surface DO minima are a common feature found in many productive regions, particularly in the non-oligotrophic regions. Below the euphotic depth a decrease in DO is observed due to consumption by the respiration and remineralization of organic matter.

Oxygen minima are a characteristic feature of many marine areas and are due to an *in situ* consumption of oxygen or to less oxygenated waters advected into the area. One example is the DO minimum zone (OMZ) in the Alboran Sea related to the LIW core (Packard et al., 1988) or the OMZs of the tropical Atlantic and the equatorial Pacific (Stramma et al., 2008). There is a small amount of oxygen consumption in the deep waters. Therefore, the DO distribution has been used as a non-conservative tracer to identify the pathway of water masses around the ocean basins or to qualitatively indicate its age, defined as the time elapsed since the fluid was at the surface (Jenkins, 1987). In practice, a quantitative calculation of the age from the DO concentrations is rarely performed, as it requires assumptions to be made regarding the consumption of oxygen, along with the exact paths of the fluid parcels and interior mixing (Stratford et al., 1998).

The objective of this work is to describe the spatial distribution and seasonal and interannual behaviour of the DO around the Balearic Islands. Keeping this aim in focus, after presenting the available data, we will first describe the spatial distribution of the DO along the Spanish Mediterranean Coast followed by a discussion of the main features of the DO in the different water masses and their seasonal evolution, computing the seasonal mean values at four representative positions around the Balearic Islands. The interannual variability of the DO at the different water masses will be discussed using the data obtained from a deep station at Cape Palos between the summer of 2007 and the autumn of 2011. Finally, the seasonal evolution of dissolved oxygen of biological origin will be considered.

2. Material and methods

The data used in this study were obtained over the course of several projects developed by the Spanish Institute of Oceanography (IEO) and are compiled under the IBAMar database (Aparicio et al., 2012). The spatial coverage extends from the Alboran Sea to Cape Creus, including the Balearic Islands. The period used in this study extends from 2001 to 2011 and the data correspond to the following projects, viz., TUNIBAL (Alemany et al., 2010), IDEA (López-Jurado et al., 2008), IDEADOS (Massutí et al., 2013), CIRBAL and RADMED (Amengual et al., 2010), which had been developed within the area using a similar strategy and methodology for the data collection. This spatiotemporal range facilitates the observation of the differences in the spatial and temporal distribution of the DO content in the different water masses.

The dissolved O_2 concentration measured will hereafter be referred to as DO. The hydrographic data were recorded using different CTDs, SBE911 and SBE25, operating at a sampling rate of 24 and 8 Hz, respectively. A SBE43 sensor with a redesign of a Clark polarographic membrane was used to record the DO. The CTDs were lowered at an average speed of less than 1 m s^{-1}. The salinity (S), potential temperature (θ) and the DO were processed using the Sea-Bird Electronics Data Processing routines. The salinity and DO concentration were calibrated on board using the water samples, whenever available. The DO determinations were performed by the Winkler titration method (Strickland and Parsons, 1972). The water samples were available when the SBE911 with a Rosetta was used (70 % of the cases presented in this work). Calibration was performed for selected depths of the water column at least once, when the campaign was less than a week, and done at least at the beginning and at the end of the campaign, when it was longer. During the TUNIBAL campaigns, the calibrations were done every three days. The spare SBE25 were cross-calibrated with a SBE911 and Rosetta at least once every campaign. Under extreme pressure, changes can occur in the gas permeable membranes which affect their permeability characteristics. Some of these changes have long-term constants and depend upon the sensors time-pressure history. These slow processes result in hysteresis in long, deep casts. Strictly following the SBE recommendations it is possible to correct this effect (SBE43, 2013). When the Rosetta samples were not available, the potential drift with time in the SBE43 was estimated using the previous and posterior campaign calibrations. Taking into account the sensor evolution between the campaigns and the available calibrations, the DO uncertainty is estimated to be 0.1 ml l^{-1}. Although the DO units of μmol kg^{-1} are often used in oceanography, the results will be presented in ml l^{-1} to help the comparison with the available climatologies (Manca et al., 2004) and previous works (Miller, 1970; Packard et al., 1988; Garcia et al., 2006). Conversion from ml l^{-1} to μmol kg^{-1} is easily done using the water density available (SBE43, 2013).

The O_2 gas solubility, O_2*, is the O_2 concentration (ml l^{-1}) calculated as a function of *in situ* temperature and salinity, at atmospheric pressure. The O_2* values were calculated using the SBE routines (SBE43, 2013; Garcia and Gordon, 1993). The oxygen saturation, O_2^S (%), was calculated as the percentage of the DO over O_2*. Apparent Oxygen Utilisation, AOU (ml l^{-1}), was calculated as O_2*− DO. The AOU is an estimate of the O_2 utilised due to biochemical processes relative to the solubility value (Garcia et al., 2006) and may be more informative regarding the age of the water mass.

Fluorescence data, obtained with a WET Labs ECO fluorometer, provide an indication of the chlorophyll-α concentration (Cullen, 1982). It will also be shown, if available and if it helps the discussion, without any calibration but with an offset correction (one for each campaign) to achieve zero fluorescence level at 1000 to 1500 dbar.

One of the aims of this study is to highlight the evolution of the DO content in the different water masses, along their path in the Western Mediterranean basin. Therefore, the study is focused on those hydrographic stations that have been visited more often, ensuring that their distribution was representative of the whole study area and reached the deep waters.

3. Results

The RADMED-1007 campaign conducted during October 2007 is used to characterise the DO distribution along the Mediterranean Spanish coast, from Barcelona to Gibraltar. This particular campaign was chosen because all the deep stations were visited and S, θ and DO are all available. The station locations are shown in Fig. 2. The stations selected are at Barcelona (115), Ibiza channel (25 and 16), Cape Palos (145), Cape Gata (155), Sacratif (165), Málaga (185) and Cape Pino (194). Fig. 3 shows the DO and vertical profiles of fluorescence of the stations selected, together with their $\theta - S$ diagrams. The surface values are not shown in the $\theta - S$ diagram. The maximum DO values, $\approx$ 5.8 ml l^{-1} (AOU $\approx$ - 0.5 ml l^{-1}, $O_2^S \approx$ 111 %) at $\approx$ 50 dbar correspond to stations 25 and 16 in the Ibiza channel. The vertical profiles of temperature, not displayed, reflect a surface mixed layer between 10 dbar and 20 dbar and a thermocline of temperature decreasing from $\approx$ 18 °C to 22 °C at 20 dbar to $\approx$ 14 °C at 100 dbar. The minimum DO values oscillate between $\approx$ 4.0 ml l^{-1} (AOU $\approx$ 1.8 ml l^{-1} , $O_2^S \approx$ 70 %) at station 115 (Barcelona) and $\approx$ 3.2 ml l^{-1} (AOU $\approx$ 2.6 ml l^{-1} , $O_2^S \approx$ 55 %) at station 194 (Cape Pino, in the Alboran sea) between the 300 to 600 dbar, around the LIW core, shown in the $\theta - S$ diagrams. The DO values increase at depths corresponding to the deep waters, and oscillate between $\approx$ 4.5 ml l^{-1} (AOU $\approx$ 1.3 ml l^{-1} , $O_2^S \approx$ 78 %) in station 115 (Barcelona) and $\approx$ 4.3 ml l^{-1} (AOU $\approx$ 1.5 ml l^{-1} , $O_2^S \approx$ 74 %) in station 145. The fluorescence profiles show a subsurface fluorescence maxima at $\approx$ 60 dbar 70 dbar, indicating the presence of a deep chlorophyll-α maximum, DCM (Estrada, 1996), in all the stations, except for stations 185 and 194 in the Alboran sea, where the maximum fluorescence values reach the surface.

Fig. 4 shows the vertical profiles of the DO and AOU data from three IDEA campaigns, Idea0204 (winter), Idea0404 (spring) and Idea0604 (summer) and their corresponding $\theta - S$ diagrams. To characterise the possible differences between the Balearic and the Algerian sub-basins, black lines are used to indicate stations 34 to 45 (north of the sampling area) and grey lines are employed to show stations 1 to 17 (south of the sampling area) as seen in the map. Table 3 shows a summary of the O_2^S and AOU values calculated for this Fig. at the depths corresponding to the different water masses.

During Idea0204, corresponding to February 2004, the surface DO values are seen to be close to saturation $\approx$ 5.6 ml l^{-1} . Below the surface, between 80 dbar and 130 dbar the relative DO maxima are also close to saturation values. At $\approx$ 500 dbar there are absolute DO minima, $\approx$ 3.8 ml l^{-1}, while at the bottom the DO values observed are slightly increased showing $\approx$ 4.2 ml l^{-1} in the Balearic sub-basin and $\approx$ 4.0 ml l^{-1} in the Algerian one. The $\theta - S$ diagrams for Idea0204 show the absence of WIW in the region sampled, although some possible episodes of intermediate convection appear as a sudden θ reduction (up to $\approx$ 0.3 °C) in the different stations, mainly in the Balearic sub-basin (black lines).

The Idea0404 campaign, occurring during April 2004, shows surface DO values that reach saturation $\approx$ 5.5 ml l^{-1}. Below the surface at around 150 dbar relative DO maxima of $\approx$ 5.3 ml l^{-1} are noted. Between 400 dbar and 500 dbar absolute DO minima of $\approx$ 3.9 ml l^{-1} are seen, and at the bottom, the DO show values of $\approx$ 4.1 ml l^{-1} in the Balearic sub-basin. The $\theta - S$ diagrams for Idea0404 show the absence of the WIW in the region sampled, strictly considering the θ and S ranges, although the scattered episodes of intermediate water formation accumulate water showing θ values slightly above 13 °C, very close to the ranges that characterise the WIW in the area.

Finally, the Idea0604 campaign, running during June 2004, shows the surface DO values that reach saturation ≈ 4.8 ml l^{-1} and a sub-surface value of ≈ 40 dbar, with supersaturation up to ≈ 6.3 ml l^{-1}. Below the surface, at around 150 dbar, relative DO maxima of ≈ 5.1 ml l^{-1} are seen. Between 400 dbar and 500 dbar there are absolute DO minima of ≈ 3.9 ml l^{-1}, while close to the bottom the DO show values of ≈ 4.1 ml l^{-1} in both the Balearic and the Algerian subbasins. The $\theta - S$ diagrams for Idea0604 show the presence of WIW in both the sub-basins revealing θ below 13 °C.

Using the IBAMar database it was possible to compute the seasonal mean values of θ, S, DO and AOU at four reference points: the Menorca deep station, to characterise the Provenzal sub-basin (station 88 in Fig. 2), the Cabrera deep station for the Algerian sub-basin (station 66 in Fig. 2), and the Ibiza and the Mallorca channels. These two describe the interchanges between the Balearic and Algerian sub-basins (stations 25 and 33 in Fig. 2). The mean values were calculated using the data from campaigns running from October 2001 to October 2011. The curves shown in Fig. 5 are a mean value of at least three vertical profiles, in winter, and up to 20, in spring and summer. The Fig. shows the vertical profiles of the AOU mean values at the stations selected for winter, spring, summer and autumn and their $\theta - S$ diagrams.

In Fig. 6 the horizontal sections of the DO at 400 m, around the LIW core depth, and at 800 m depth, about the interface with the DWs are shown.

The plots correspond to December 2009 and June 2010 IDEADOS surveys. During December 2009, the north DO values are around 4.20 ml l^{-1} and 4.37 ml l^{-1} at 400 m and 800 m, respectively, while the south DO values are around 4.05 ml l^{-1} and 4.27 ml l^{-1} at 400 m and 800 m, respectively. During June 2010, the north DO values are around 4.05 ml l^{-1} and 4.27 ml l^{-1} at 400 m and 800 m, respectively, while the south DO values are around 4.05 ml l^{-1} and 4.20 ml l^{-1} at 400m and 800m, respectively.

Cape Palos (RADMED stations 143 and 144 in Fig. 2) has been chosen to characterise the seasonal evolution of the AOU cycle in the intermediate and deep waters (Figs. 7 and 8) because it has a stable circulation pattern. It is found in the Algerian sub-basin, far away from the areas of WMDW and WIW formation, a fact that helps to smooth out the strong seasonal variability observed in the formation events in the Balearic sub-basin. Cape Palos was sampled every season (every three to four months), from the summer of 2007 to the autumn of 2011. The data include the potential temperature (θ), salinity (S), AOU and potential density (σ_θ). When the interest focuses on the surface and intermediate waters, station 143 is used for clarity, because more AOU data are available there, although the results are similar for both stations. In Fig. 7 the variables are plotted from the surface to 500 dbar and down to 2000 dbar in Fig. 8. To smooth the high frequency oscillations, data were interpolated into a regular grid every 15 dbar and 45 days.

In Fig. 9 the annual cycle of O_2^S and fluorescence from 0 to 150 dbar, using the IBAMar database are seen. The stations have been chosen to lie between longitude 1°E and 5°E and latitude 38°N and 45°N. Only stations with a bottom depth greater than 300 m were considered, to avoid coastal effects. Although more than 1400 stations exist within these requirements no data is available from the middle of December to the middle of February. To smooth the statistical oscillations, data were interpolated into a regular grid every 5 dbar and 5 days. The fluorescence around the Balearic Islands is observed to be very patchy. Although some (very few) stations do exhibit a fluorescence maxima up to 8 mg m^{-3} the smoothed signal maximum values hover around 1 mg m^{-3}.

4. Discussion

4.1. Spatial distribution of dissolved oxygen (DO) along the Spanish Mediterranean Coast

Vertical profiles of DO (Fig. 3) show the presence of a subsurface ($\approx$ 50 dbar) maximum of up to 5.8 ml l^{-1} (AOU $\approx$ -0.5ml l^{-1}, $O_2^S \approx 111$ %) in all the stations except 194 and 185 in the Alboran sea. This maximum is within the thermocline (from 20 to 100 dbar) and appears $\approx$ 10 dbar 20 dbar above the DCM. There is no exchange with the atmosphere due to the strong stratification, and the supersaturation therefore is due to the biological activity (e.g Deya-Serra, 1978). Stations 194 and 185 show a surface maximum of fluorescence, related to the phytoplankton blooms usually observed, due to wind driven upwelling events in this area. In those stations, the sub-surface DO maximum, related to the DCM, is not observed because there probably is a net flux of DO of biological origin from the sea into the atmosphere.

At 400 dbar, a clear DO minimum is observed corresponding to the LIW core (see Tables 1 and 2). The values of DO observed at the LIW are $\approx$ 0.5 ml l^{-1} to 0.8 ml l^{-1} lower than the climatological values reported by Manca et al. (2004). Below the LIW, the WMDW show a relative increase in the DO corresponding to the incorporation of the recently formed DW.

The LIW and WMDW values of DO clearly decrease from Barcelona to Gibraltar. This reduction is in agreement with the DO depletion during the remineralisation of the organic matter at greater depths in the water column (Chester, 2000) combined with the southward advection of the intermediate and deep waters along the continental self (Millot and Taupier-Letage, 2005). This is an indication of the increasing age of the intermediate and deep water masses as they progress southwards. Font (1987) indicates that the winter velocities in the intermediate layer are in the order of 5 cm s^{-1} and he argues that if this velocity were maintained the whole year through, the LIW would cross the Balearic Sea in about three months, and the LIW outflow through the Ibiza sill would reach the Alboran Sea two months later. If it is assumed that those velocity values are maintained constant during the year, that the LIW path is well determined along the continental slope and that there are no significant vertical mixing effects, the oxygen consumption rates would be of the order of 1-2 ml l^{-1} yr^{-1} (from the AOU reduction observed in Fig. 3) which is much higher than the values reported for the Mediterranean (e.g. Souvermezoglou et al., 2002). This enables us to conclude that any of the hypotheses mentioned earlier are inaccurate. Therefore, it is reasonable to argue that the LIW velocity does not remain constant throughout the year and that the LIW which arrives at the Alboran Sea does not follow well-defined paths and probably the advection time is longer than the values deduced by Font (1987).

Oxygen Minimum Zones (OMZ) can be big phenomena. Packard et al.

(1988) suggested that the OMZ observed in the Alboran Sea is the result of a chain of processes, commencing with the nutrient enrichment of the Atlantic water flowing into the Mediterranean, increased by the nutrient rich water that rises by upwelling along the Spanish coast where the phytoplankton blooms occur. The blooms are transported to the convergence zone in the centre of the Alboran gyre, which acts as a plankton trap. Dead plankton and faecal material rain down into the LIW, where they are metabolised by the bacteria, a process which consumes oxygen and maintains the most intense OMZ in the Mediterranean Sea with values reported to be about 3.5 ml l^{-1} (Packard et al., 1988) . In Fig. 3 the minimum DO values of $\approx$ 3.2 ml l^{-1} in the Alboran Sea (stations 185 and 194) are shown, corresponding to the LIW core.

A sea surface temperature (SST) trend from 20 °C in 1985 to 21 °C in 2005 has been reported in the eastern Mediterranean basin (Nykjaer et al., 2009) where the LIW is formed. This trend will decrease the oxygen solubility O_2* in the eastern basin by less than 0.1 ml l^{-1}. However, this reduction in the SST is not enough to explain the DO reduction observed in the LIW in the OMZ in the Alboran Sea. Other scenarios may affect the amount of new production in the region (and therefore the DO depletion in the lower waters), such as the changing wind regimes which may change the timing, duration and intensity of the blooms, finally affecting the DO in the OMZ. More DO measurements together with the nutrients and atmospheric data are essential to clarify if the reduction in the DO observed in the Alboran OMZ is a fluctuation that occurs within the statistics, a global warming effect as has been suggested for the Atlantic and Pacific OMZs (Stramma et al., 2008; Shaffer et al., 2009), an anthropogenic effect due to the increase in the nutrients in the river discharges that modify the new production (Bethoux, 1989) or if it is due to other scenarios that may be induced by a modified climate (Diaz and Rosenberg, 2008).

4.2. Seasonal variability of dissolved oxygen around the Balearic Islands

The vertical distribution of the DO around the Balearic Islands show pronounced features, related to the different water masses, which can be observed in the data presented in Fig. 4.

The DO in the surface layer is due to the exchange with the atmosphere and its concentration is mainly determined by the SST. Around the Balearic Islands the maximum DO values are observed at the surface in winter, when these values can be as high as 5 to 6 ml l^{-1}. During the summer, the surface DO values are reduced by 1 to 2 ml l^{-1}, due to the higher SST (Fig. 4 Idea02014 and Idea0604). The surface DO values are close to saturation during the three Idea campaigns, as shown in Table 3. Oxygen is released during photosynthesis, although this process is restricted to the upper water column. In this area the usual limit of photosynthesis lies within the upper 100 m. The exchange of photosynthetic DO with the atmosphere can be blocked due to the summer stratification with the result that the process of photosynthesis produces the oxygen supersaturation. Around the Balearic Islands this subsurface DO maximum ranges between 40 and 80 dbar and up to 6.5 ml l^{-1} (Fig. 4 Idea0604) with $O_2^S \approx 116$ % (Table 3). Below the zone where the photosynthesis occurs, a decrease in the DO is noted owing to its biological consumption. Around the Balearic Islands this absolute minimum is observed at the core of the LIW at around 400 dbar and it is usually noted to be below 4 ml l^{-1} (Fig. 4) being $O_2^S \approx 66$ % constant during the three Idea campaigns (Table 3). This is probably due to the very little oxygen consumption at these depths that makes the DO appear constant during the four months sampled. The DO concentrations usually show a gradual increase from the minimum layers to the bottom of the water column. This is a result of the deep water formed during the deep convection events in winter when the surface and ventilated waters sink to the bottom. The recently formed and ventilated DW is being advected from the Gulf of Lions driving the DO increase thus observed, with depth. Once the ventilated water mass has sunk to the bottom, the DO consumption occurs by the biological activity. As this DO cannot be refilled by exchange with the atmosphere or by photosynthesis, the DO concentrations decrease with distance from the source. The deep waters are observed to present more DO to the north of the Balearic Islands than to the south in winter, (Fig. 4 Idea0204) with a difference of O_2^S of ≈ 1 % (Table 3). This difference could be due to the longer time that the WMDW needs to reach the south sampling area (grey lines) from its source along the insular slope. Amores et al. (2013) reveal average velocities from 2 to 4 cm s^{-1} at 500 m and from 3 to 7 cm s^{-1} at 900 m, at a mooring placed at the north sampling area, influenced by the Balearic Current, during the IDEADOS campaigns (Fig. 6). Under assumptions similar to those made to estimate the LIW consumption along the Spanish coast (Fig. 3), the oxygen consumption rates in winter will be of the order of 0.2 ml l^{-1} yr^{-1} closer to some values reported for the Mediterranean (Souvermezoglou et al., 2002). In any case, this difference between the north and south sampling area is observed only in the winter during 2004 and it could simply be due to the arrival of the more recent WMDW in the northern sampling area (Fig. 4).

The relative maxima of DO are also observed at around 150 dbar in the winter and spring. Each relative DO maximum corresponds to a θ reduction observed in the $\theta - S$ diagram (Fig. 4 Idea0204 and Idea0404). Those DO maxima reflect the recently formed and ventilated intermediate water lenses that develop during different intermediate convection episodes (Vargas-Yáñez et al., 2012). In the summer profile (Fig. 4 Idea0604) only one relative maximum is noted, that appears to be due to the aggregation and homogenisation of the intermediate water lenses. The WIW is clearly observed in the corresponding $\theta - S$ diagram.

The main seasonal features of the AOU can be observed in the different water masses in Fig. 5. The surface water is close to saturation, AOU ≈ 0 ml l^{-1}, during the four seasons. In the spring, there is a gradual increase in the temperature and the first appearance of summer subsurface oxygen supersaturation (AOU negative) due to photosynthetic activity and the beginning of stratification (Fig. 5 spring) is noted. In the summer, the DO at the surface decreases, due to the increased SST and equilibration with the atmosphere, although the subsurface DO maximum is reinforced due to biological activity, revealing AOU concentrations as low as -0.5 ml l^{-1}. This AOU minimum (DO maximum) is always slightly above the DCM (not shown), (Deya-Serra, 1978), and sometimes the DO is observed to reach values up to 6 to 7 ml l^{-1}. In the autumn the supersaturated structure is maintained with less intensity although in the late autumn and winter, the atmospheric forcing breaks the stratification producing a homogenisation of the surface waters that equilibrate close to saturation (Fig. 5, winter). In the winter, the clear influence of the recently formed WIW is seen, with a relative AOU minimum (DO maximum) between 100 and 300 m, as is observed at station 25 in the Ibiza Channel, where each relative minimum corresponds to different formation events (Fig. 5, winter). The years when the WIW formation occurs, it is more homogeneously observed during the spring and summer seasons, mainly at station 25 at the Ibiza channel, but also at station 33 at the Mallorca channel when the WIW is advected with the Northern Current from its origin. This behaviour is smoothed in Fig. 5 (spring and summer) due to the averaging of the years with WIW formation and years with WIW absence. During the autumn the recently formed WIW is not present in the area (Fig. 5, autumn). Maximum AOU values related with the LIW core, from 400 dbar to 600 dbar, appear to increase ≈ 0.1 ml l^{-1} from spring to winter. Below the LIW an expected AOU decrease is seen with the depth corresponding to the more recent formation of the WMDW.

4.3. Deep water advection around the Balearic Islands

The horizontal sections seen in Fig. 6 reveal that during December 2009, the north DO values are around 0.1 to 0.2 ml l^{-1}, higher than the south values both at 400 m depth (Fig. 6A) and 800 m depth (Fig. 6B). During June 2010, the north and south DO values are comparable at 400 m depth (Fig. 6C) but at 800 m depth (Fig. 6D) they are again 0.15 ml l^{-1} higher in the north. There is a north-south difference in the DO values at 800 m depth, both during December 2009 and June 2010, already been discussed prior in terms of deep water advection (Fig. 4 Idea0204). The deep water produced in the winter during the deep convection events in the Gulf of Lions cannot cross the Ibiza and Mallorca channels advected with the Northern Current because the channel sills are only 800 m and 700 m in depth, respectively. Therefore, it gets advected around the Balearic Islands with the Balearic Current along the continental slope. This advection is observed as a decrease of the DO in the deep waters from the north to the south of the Islands (Fig. 6 and Fig. 4).

It has also been discussed how the absolute DO minimum is observed at the core of the LIW at around 400 m (Fig. 4) being $O_2^S \approx 66$ % constant during the three Idea campaigns (Table 3). In those cases it was argued that this is probably due to the very little oxygen consumption at these depths that makes the DO appear constant during the four months sampled. The case of December 2009 at 400 m (Fig. 6 A) does not concur with that argument because it shows a north-south difference at 400 m depth of more than 0.2 ml l^{-1} (Fig. 6A). This increase in the DO observed in the north of the sampling region can be explained in terms of an oceanic front that was detected during the survey from the surface down to 400 m depth. This front caused upward vertical velocities of 6 m day^{-1} (Balbín et al., 2012). These intense upward velocities brought the lower and DO richer waters up from down above.

4.4. Seasonal evolution of apparent oxygen utilisation at Cape Palos

To better understand the seasonal evolutions of AOU at Cape Palos (stations 143 and 144 in Fig. 2), the presence or absence of the different water masses must be examined throughout the year and, in particular, the depths they occupy. The annual cycle of seasonal thermocline formation and collapse is clearly observed in Fig. 7. Isopycnals shallower than 28.6 kg m^{-3}

begin to descend during the spring, reaching their maximum depth in the autumn and ascend, outcropping even the surface, during winter. The isopycnal 28.0 kg m^{-3} occasionally ventilates at the end of the winter, as in 2010. Subsurface waters display the spring-summer oxygen supersaturation (AOU below 0 ml l^{-1}) due to the photosynthetic activity in the DCM within the thermocline.

Using the temperature and salinity patterns it is possible to observe the presence of WIW, with $\theta \leq 13$ °C and $S \geq 38.3$ (Table 1). From the data at stations 25 and 16 (Balbín et al., 2013) it is evident that the WIW was present in the Ibiza channel every year, except 2007, although its presence was observed at Cape Palos only during 2009, 2010 and 2011 (Fig. 7). In 2009 and 2011, the WIW was advected by the Northern Current, across the Ibiza channel, arriving at Cape Palos during the spring and summer. During the winter of 2010, the WIW formation was observed as far to the south as Cape Palos (Vargas-Yáñez et al., 2012). This fact is noted clearly in the temperature pattern of Fig. 7 which shows the higher volume occupied by the WIW during 2010, which appeared during the early winter that year. The events producing the WIW formation lead to even stronger ventilation, which is observed as the relative AOU minima $\approx$ 0.4 - 0.6 ml l^{-1} for the years 2009, 2010 and 2011 (Fig. 7).

The depth of the interface with the LIW, $S \geq 38.40$, deepens during the spring and summer (earlier in 2010) when the recently formed WIW spreads over the LIW (Fig. 7). If the AOU is used as a water mass tracer, it can be deduced that the LIW core is associated with the AOU $\geq$ 1.8 ml l^{-1}. Using the AOU it is possible to observe the intermittent presence or absence of the

LIW cores that are observed at Cape Palos usually during the autumn and winter. The nucleus of the LIW can be observed intermittently at around 400 to 500 dbar as the salinity maxima and AOU minima in Fig. 8.

The interphase between the LIW and WMDW can be defined by the 38.48 isohaline and 12.9 °C isothermal around or below 1000 dbar in Fig. 8. The depth of this interphase oscillates with time without a clear seasonal behaviour. The AOU and density patterns of Fig. 8 are well correlated in the deep waters, indicating that the denser waters are more ventilated and therefore more recent.

At around 1500 dbar it became possible to observe the indications of the thermohaline anomaly in the WMDW which appeared in 2005 (López-Jurado et al., 2005). This anomaly was due to the exceptional amount of DW formed during the 2005 winter and its causes are still unclear. Major changes observed in the western Mediterranean deep water include an abrupt increase in the deep heat and salt contents, when the isopycnals were lifted up hundreds of metres accompanied by the appearance of a sharp inversion in the $\theta - S$ diagrams (Schroeder et al., 2012). This inversion in θ and S can be observed as the relative maxima at $\approx$ 1500 dbar in Fig. 8. Those relative maxima in θ and S appear intermittently every year. Their relatively higher AOU $\approx$ 1.4 - 1.6 ml l^{-1}, indicate that those waters are older than the deeper ones.

4.5. Seasonal evolution of dissolved oxygen of biological origin

It is interesting to know the timing and progress of the DO of biological origin because the annual cycle is a dominant mode of variability in the biology and chemistry of the ocean (Najjar and Keeling, 1997). In Fig. 9 the annual cycles of O_2^S and fluorescence around the Balearic Islands are seen. The fluorescence data helps to visualise the seasonal cycle of the euphotic depth, driven by the solar flux at the surface, so that it is at its greatest in the early summer and its least in winter. The fluorescence signal starts to become well defined in early spring, occupying the whole photic layer. The signal deepens during the spring and early summer and ascends during the late summer and autumn. Around April the surface fluorescence vanishes, probably due to the depletion of the surface nutrients, and an intense subsurface maximum appears. The O_2^S data shows that the oxygen within the mixed layer is close to the saturation concentration. Supersaturation is observed in the summer when the net community production is higher. In the waters below the mixed layer, the photosynthetically produced oxygen cannot escape to the atmosphere due to the strong stratification within the seasonal thermocline. This results in the subsurface oxygen supersaturation observed in the data between June and October. The supersaturation vanishes when the winter atmospheric forcing breaks the stratification and deepens the mixed layer, which leads to oxygen concentrations close to saturation. Maximum O_2^S are always observed slightly above the subsurface fluorescence maximum.

5. Conclusions

To our knowledge there are very few published results on the DO characteristics around the Balearic Islands except for the work of Deya-Serra (1978). Manca et al. (2004) have done a climatological description of the DO on the Gulf of Lions while there are also some data collections close to the Balearic Islands (Miller, 1970) and several works on the OMZ of the Alboran

Sea (e.g. Packard et al., 1988). This, however, is the first work trying to make a characterisation on the DO considering all the information together, along the Spanish Mediterranean coast including the Balearic sub-basin, the Algerian sub-basin and the Alboran Sea.

The DO values observed around the Balearic Islands are in general concurrence with the prior climatology data as shown in Table 2 (Manca et al., 2004) and the earlier studies (Miller, 1970) except for the minimum DO values observed within the LIW cores and the relative maximum related with the WIW. The surface DO values oscillate between 6 ml l^{-1} in winter and 4.5 ml l^{-1} in summer. In spring and summer a subsurface oxygen supersaturation due to biological activity is noted up to 6 to 7 ml l^{-1}. The relative maxima of the DO at 150 dbar are observed from winter until summer in the Ibiza and Mallorca channel related to WIW recently formed. The minimum DO values related to the LIW core, from 400 dbar to 600 dbar, appear to decrease from spring until winter, staying below 4.0 ml l^{-1} around the Balearic Islands. Below the LIW the expected DO increase with depth is seen, corresponding to the more recent formation of the deep waters.

The interannual variability accounts for unusual minima DO concentrations in the LIW, and minimum DO values below those reported by Packard et al. (1988) in the Alboran Sea OMZ. More data regarding DO measurements as well as on the nutrients and atmospheric variations are needed to clarify the reason for the DO observed in the Alboran Sea.

The DO concentrations and AOU are good indicators to detect the events of WIW and WMDW formation and their advection along the continental slope. The LIW and WMDW DO concentrations decrease along their path due to biochemical consumption. Using the arguments of oxygen consumption it is possible to qualitatively show that the WIW propagates southwards with the Northern Current, mainly across the Ibiza Channel and the WMDW circulates with the Balearic Current, following an along-slope path around the Balearic Islands, requiring a longer time to arrive to the south of the islands. Accordingly, the DO concentrations below 800 m are 0.15 to 0.20 ml l^{-1} higher in the north of the Balearic Islands than in the south, and this difference is better observed in the winter.

It is possible to characterise the seasonal evolution of the different water masses and their AOU cycle in a station at Cape Palos. The seasonal thermocline formation and collapse are observed in the surface waters, while the sub-surface waters show the spring-summer oxygen supersaturation due to photosynthetic activity. Some of the years show the WIW (with its associated AOU relative minimum) appearing intermittently above the LIW (with its associated AOU maximum), occupying its volume, during spring and summer. During 2010, the WIW appears earlier because it was exceptionally formed as far to the south as Cape Palos (Vargas-Yáñez et al., 2012). The depth of the interphase between the LIW and WMDW varies with time. More sampling is warranted to characterise its seasonal behaviour. The AOU and density patterns indicate that both are correlated at the deep waters indicating that the denser waters are more recent. At 1500 dbar it is possible to observe the signals of the thermohaline anomaly in the WMDW (López-Jurado et al., 2005) in the potential temperature and salinity, that are yearly intermittent. Their relatively higher AOU indicate that those waters are older than the deeper ones.

Around the Balearic Islands the subsurface fluorescence maximum depth follows the seasonal cycle of the euphotic depth and vanishes in winter. Maximum O_2^S are always observed slightly above the subsurface fluorescence maximum.

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Water mass	Values at origin	Local values
AW	$15.0 < \theta < 18.0$	$15.0 < \theta < 28.0$
	$36.15 < S < 36.50$	$36.50 < S < 37.50$
Resident AW	$13.0 < \theta < 28.0$	$13.0 < \theta < 28.0$
	$37.50 < S < 38.30$	$37.50 < S < 38.20$
WIW	$12.5 < \theta < 13.0$	$12.5 < \theta < 13.0$
	$37.90 < S < 38.30$	$37.90 < S < 38.30$
LIW	$14.0 < \theta < 15.0$	$13.0 < \theta < 13.4$
	$38.70 < S < 38.80$	$38.45 < S < 38.60$
WMDW	$12.7 < \theta < 12.9$	$12.7 < \theta < 12.9$
	$38.40 < S < 38.48$	$38.40 < S < 38.48$

Table 1: Characteristic values of the potential temperature (θ) and salinity (S) of the different water types and local values in the Balearic Sea (López-Jurado et al., 2008)

Water mass	Temperature (°C)	Salinity	Oxygen (ml l^{-1})
Gulf of Lions			
Surface water (0-5 m)	17.61±2.30 (14,218)	37.88±0.45 (9472)	5.44±0.24 (2182)
LIW (400 m)	13.17±0.11 (3101)	38.48±0.03 (2306)	4.48±0.17 (610)
WMDW (≥ 1500 m)	13.04±0.02 (3218)	38.42±0.01 (3473)	4.60±0.07 (1214)
Alboran Sea			
Surface water (0-5 m)	17.85±0.616 (18,874)	36.57±0.28 (7122)	5.44±0.33 (1877)
LIW (400 m)	13.07±0.08 (2014)	38.45±0.04 (1588)	4.21±0.17 (320)
WMDW (≥ 1500 m)	13.08±0.03 (176)	38.44±0.01 (170)	4.50±0.09 (21)

Table 2: Spatially averaged water properties in two regions of the Western Mediterranean according to Manca et al. (2004). The average and standard deviations for the physical parameters (the quantity of data used are indicated within brackets) for three layers, which essentially characterise the water column structure.

Campaign	Idea0204		Idea0404		Idea0604	
Water mass	O_2^S	AOU	O_2^S	AOU	O_2^S	AOU
Surface water (0-5 m)	98%	0.1	100%	0	100%	0
Surface water (50-80 m)	98%	0.1	100%	0	116%	-0.7
WIW (100-200 m)	98%	0.1	90%	0.6	85-87%	0.6-0.8
LIW (400-500 m)	67%	1.9	66%	1.9	67%	1.9
WMDW (≥ 1500 m)	70-72%	1.6-1.7	71%	1.7	71%	1.6

Table 3: A resume of the O_2^S and AOU (ml l^{-1}) values for the vertical profiles in Fig. 4.

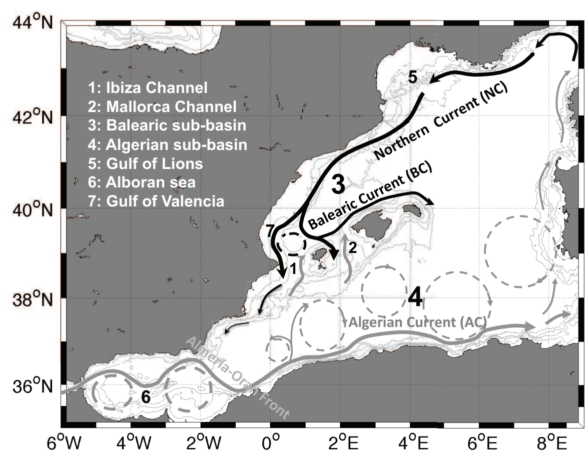

Figure 1: The Balearic Islands and the main surface currents that describe the regional circulation. The Mallorca and Ibiza channels are shown. The Northern and Balearic Currents are indicated by dark grey arrows while the Algerian gyres are indicated by light grey arrows. The light grey lines denote the isobaths (100 m, 500 m, 1000 m, and 2000 m).

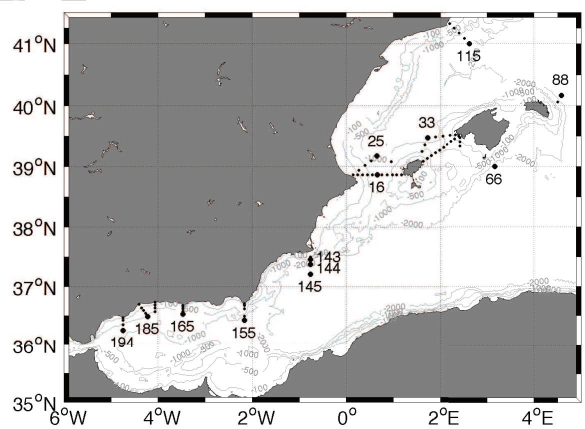

Figure 2: Distribution of the RADMED-1007 stations along the Spanish coast. Numbered black dots correspond to the stations selected for the present study.

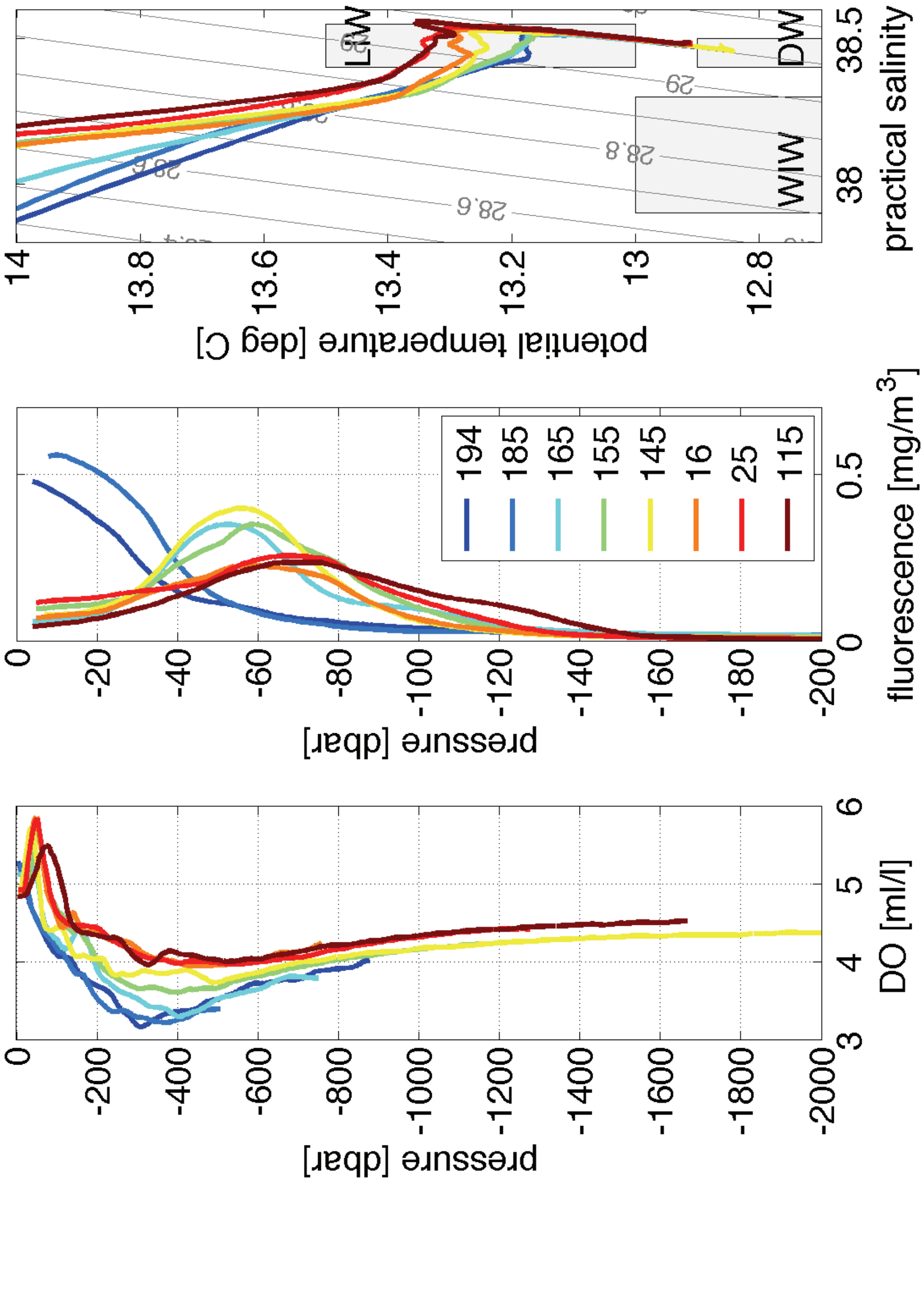

Figure 3: Vertical profiles of the DO from the surface to the bottom and fluorescence from the surface to 200 dbar at the stations along the mainland are shown in Fig. 2, with their corresponding $\theta - S$ diagrams. The grey boxes over the $\theta - S$ axis indicate the local values that characterise the different water masses as shown in Table 1.

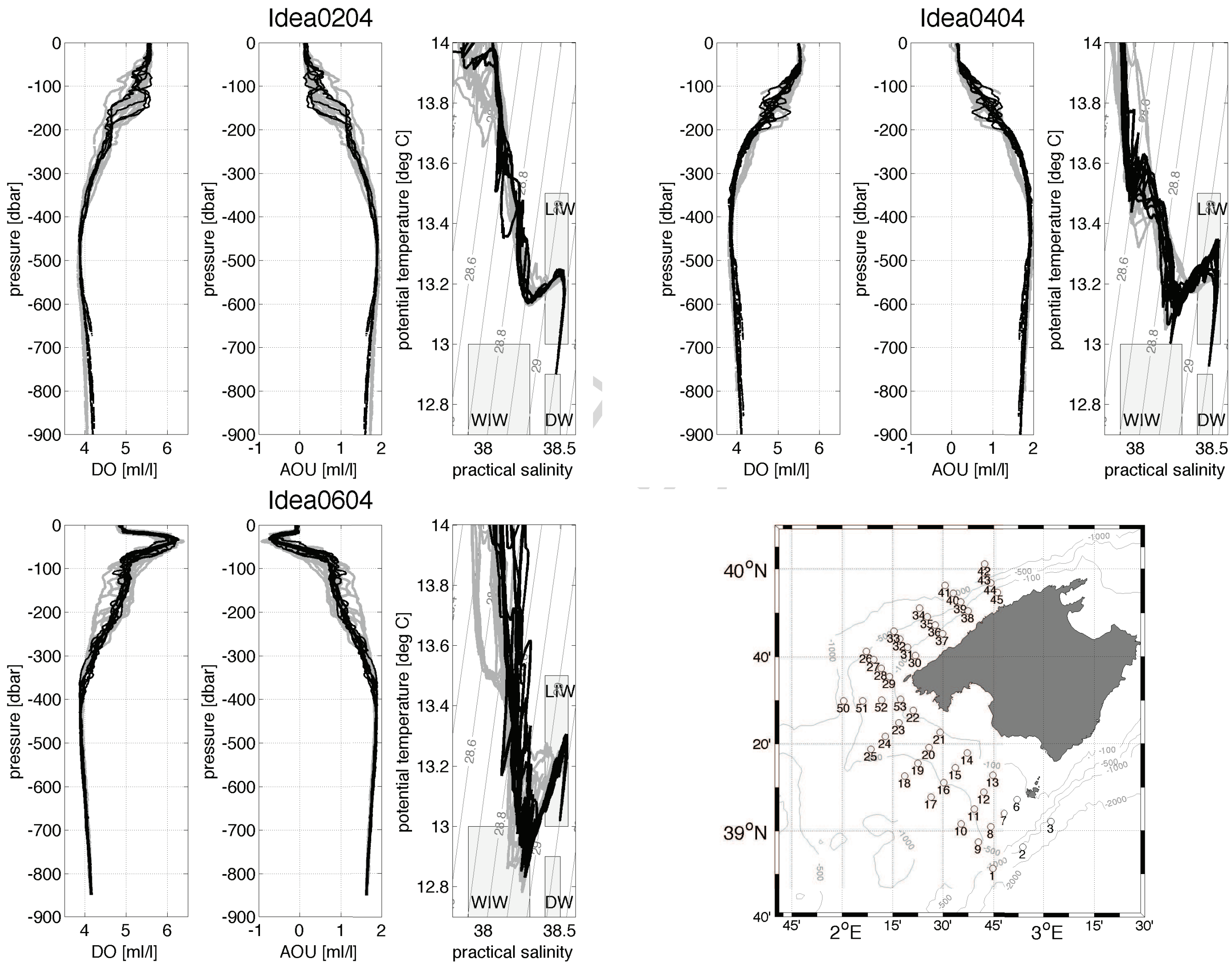

Figure 4: Vertical profiles of the DO and AOU from the surface to the bottom at the IDEA stations are shown in the map and corresponding to winter (February 2004), spring (April 2004) and summer (June 2004) and their corresponding θ-S diagrams. The black lines refer to stations 34 to 45, while the grey lines indicate stations 1 to 17 as shown in the map.

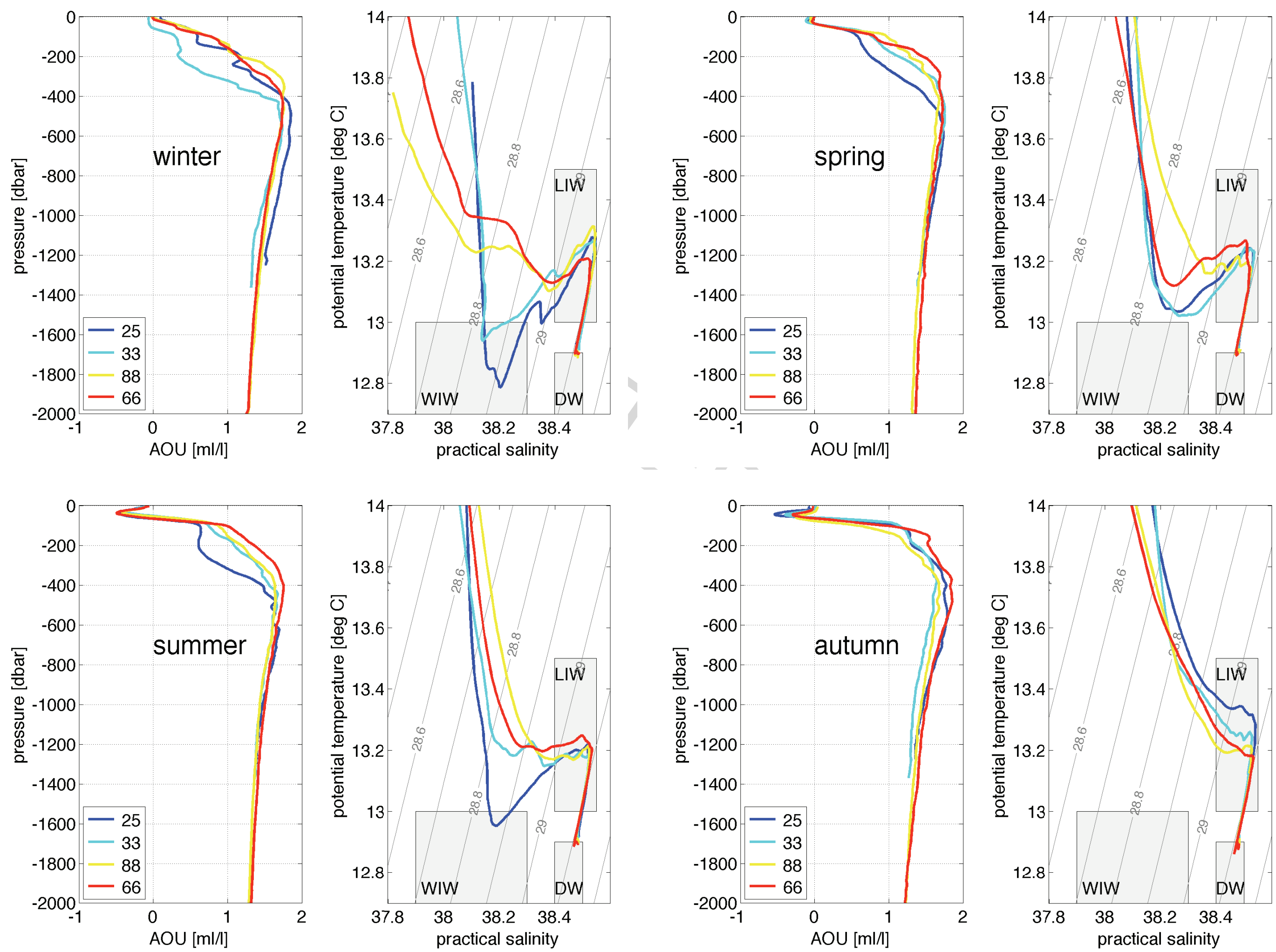

Figure 5: Vertical profiles of the AOU in ml l^{-1} from the surface to the bottom corresponding to the winter, spring, summer and autumn mean values at selected deep stations around the Balearic Islands and their corresponding $\theta - S$ diagrams. Numbers 25 and 33 are stations in the Ibiza and Mallorca channels, respectively, while numbers 88 and 66 are the deep stations in the north of Menorca and south of Cabrera, as shown in Fig. 2.

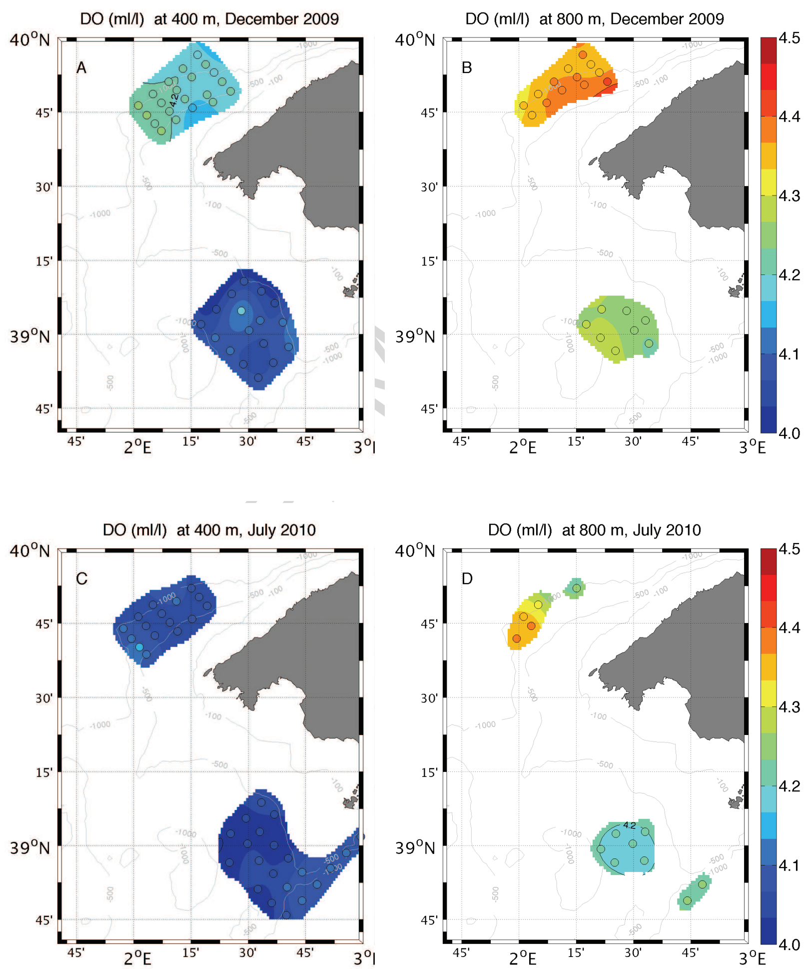

Figure 6: The DO at 400 m (A and C) and 800 m (B and D) for the IDEADOS surveys. A and B correspond to the early winter while C and D indicate the summer.

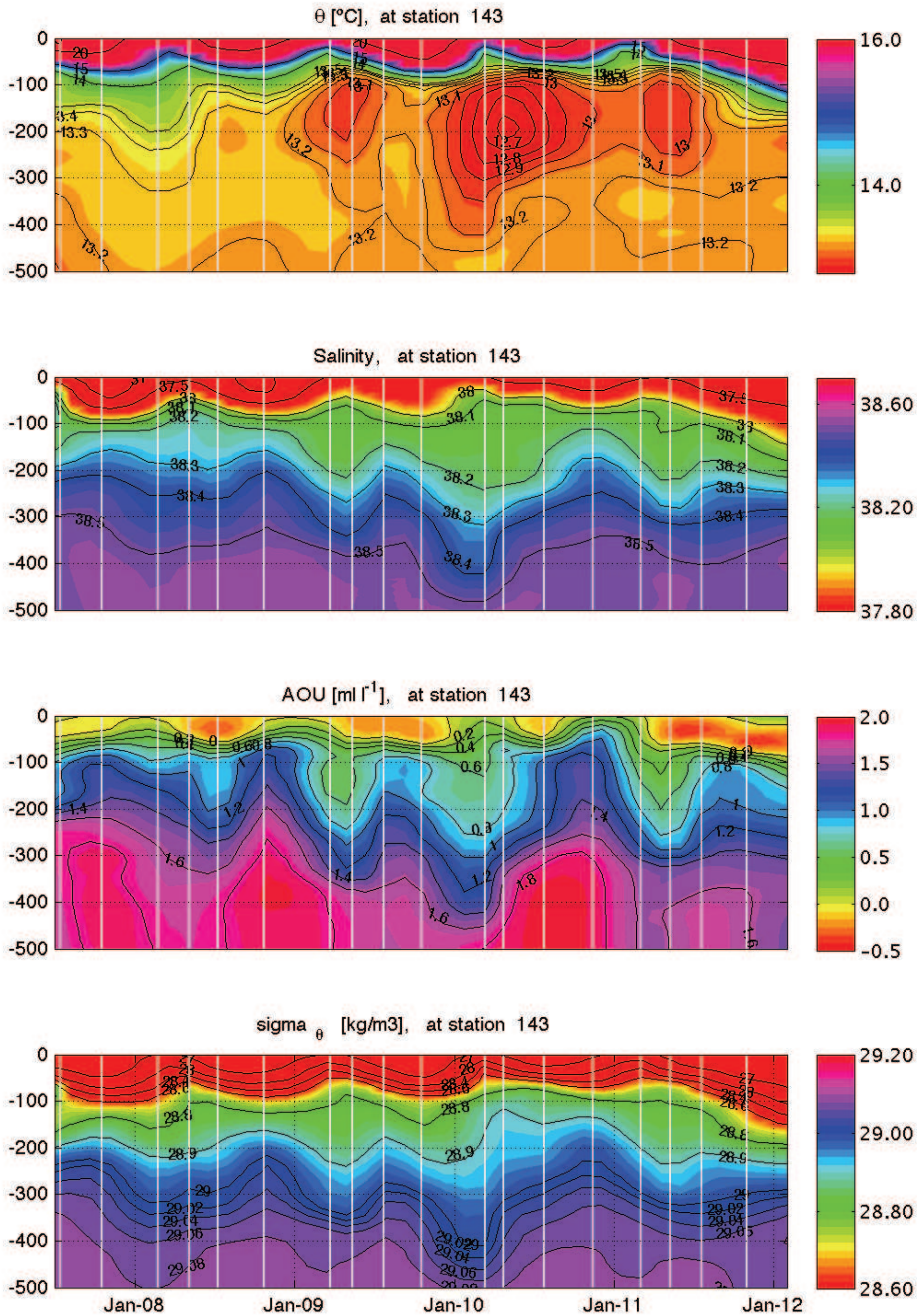

Figure 7: Temperature, salinity, AOU and σ_θ at station 143 versus pressure and time. Grey vertical lines correspond to station sampling date.

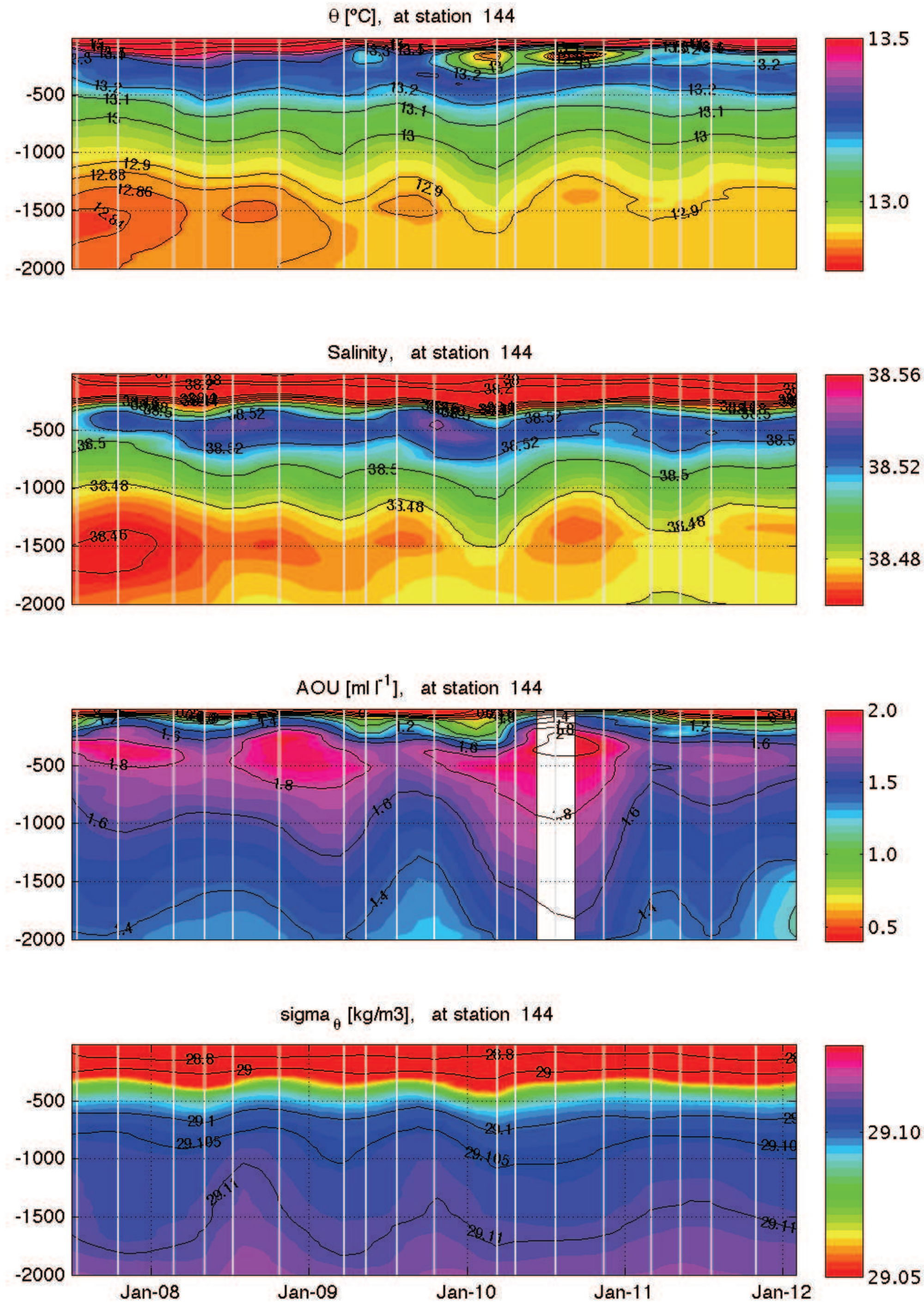

Figure 8: Temperature, salinity, AOU and σ_θ at station 144 versus pressure and time. Grey vertical lines correspond to survey date. White box indicate there were not DO data.

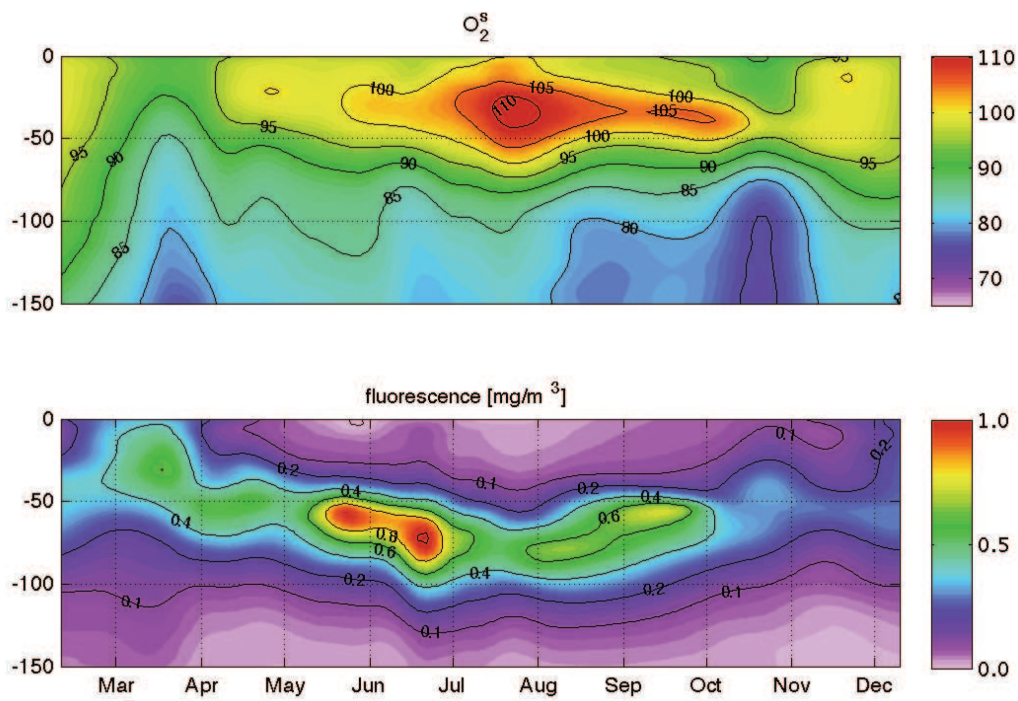

Figure 9: The O_2^S and fluorescence around the Balearic islands versus pressure and time.

Highlights

DO around the Balearic Islands are in agreement with the prior climatology data.

Minimum DO values are observed within the LIW and relative maximum within the WIW.

Maximum DO are always observed slightly above the subsurface fluorescente maximum.

DO is a indicator to WIW and WMDW formation and advection along continental slope.

The seasonal evolution of the different water masses and their AOU is described