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Intermediate water masses off south-southwest Portugal: Chemical tracers

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ABSTRACT

Biogeochemical tracers, as dissolved oxygen and nutrients, were measured during several surveys carried out between 1999 and 2001, off south-southwestern Portugal. The dense vertical and horizontal sampling allows the extensions of intermediate water masses present in the region to be resolved. A subsurface minimum salinity water layer, exhibiting values of apparent oxygen utilization (AOU) in the range 40–60 $\mu\text{mol/kg}$ and intruding into the study area mainly from the south-southwest, is proposed to be a remnant of the Subarctic Intermediate Water (SAIW). A deeper salinity minimum displaying high concentrations of nutrients and AOU ($\sim 100 \mu\text{mol/kg}$) and identified as a branch of the Antarctic Intermediate Water (AAIW), is observed to derive from the western African coast and to penetrate the area predominantly from the south-southeastern side. The salty and warm Mediterranean Water (MW) present in the same density range as the fresher intermediate waters, reveals differentiated chemical properties at the various depths depending on the surrounding waters. Analysis of water masses gives an indication that the collapse of the fresher waters into a narrow range of salinity values (35.58–35.64) at intermediate levels is favored by the strong presence of the MW outflow, and that the admixture of the fresher waters with the MW outflow very likely induces the formation, splitting and spreading of several MW cores extending westwards along the Portuguese coast.

1. Introduction

Since the early 1980's various studies have updated the hydrography of the eastern North Atlantic (e.g. Harvey and Arhan, 1988; Reid, 1994; Wade *et al.*, 1997; Paillet *et al.*, 1998). It is known that intermediate water masses influence the structure of the water column with consequences for ocean stratification. As the density ranges of intermediate waters show considerable overlap and their circulation near the continental margin is constrained by the bottom topography, the structure of these mid-depth waters is rather complex. Nevertheless, these waters carry distinct chemical signatures over long distances. So, the use of specific biogeochemical variables can be valuable in helping to disentangle the intermediate water mixtures, contributing to their characterization and identification of the respective pathways.

The intermediate freshwater mass of Antarctic origin, the AAIW, which is known to

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extend northward flowing along the African coast (Tsuchiya, 1989; Tsuchiya *et al.*, 1992; Harvey and Arhan, 1988), exhibits high apparent oxygen utilization (AOU) ($\sim 100 \mu\text{mol/kg}$) and nutrient levels ($\text{NO}_3 \sim 35 \mu\text{mol/kg}$) (Kawase and Sarmiento, 1986). Recently, there has been evidence that this water mass reaches the southwestern Iberian Peninsula (van Aken, 2000) and the Gulf of Cádiz (Cabeçadas *et al.*, 2002). The SAIW, a cold freshwater mass that originates in the western North Atlantic, creates a complex oceanic circulation and some of its remains flow toward the eastern Atlantic margin (Arhan, 1990; Arhan *et al.*, 1994). In contrast to the AAIW, this northern water mass is well-ventilated, displaying AOU values close to $60 \mu\text{mol/kg}$ (Read and Ellet, 1991) and relatively lower nutrients (Hinrichsen and Tomczak, 1993). The intermediate MW spreading from the Gibraltar sill into the Atlantic, on the other hand, shows relatively low contents of dissolved oxygen and nutrients (Ambar and Howe, 1979; Rhein and Hinrichsen, 1993; Ambar *et al.*, 2002).

There are few investigations on biogeochemical tracers of fresher intermediate waters in the region strongly influenced by the MW outflow (van Aken, 2000; Cabeçadas *et al.*, 2002). The present study addresses the identification and spreading of intermediate waters off south/southwestern Portugal using biogeochemical parameters, by means of horizontal and vertical high-resolution data analysis. Further, the mixing of these water masses is also examined.

2. Methodologies

a. Sampling, analytical procedures and calculations

A hydrographic survey was carried out in September 1999 off south-southwest Portugal along several sections totaling 76 stations (Fig. 1), sampled to a maximum of 12 depths selected in order to cover most of the water column occupied by intermediate waters. In July 2000 and October 2001 a station located at 35.97N , 8.00W (station HR) (Fig. 1) was sampled at about 50 m intervals, respectively, from 500 to 800 m in July and 700 to 1200 m in October. The aim of this high resolution sampling was to cover the intermediate water masses above the MW lower core in July, and to depict in detail the MW outflow and other intermediate water masses as well, between 700 and 1200 m, in October.

In the September 1999 survey, conducted onboard the RV *Almeida Carvalho*, vertical temperature and salinity profiles were obtained with a Neil-Brown Mark III CTD coupled to a General Oceanics rosette equipped with Niskin bottles to collect water samples for determination of dissolved oxygen (O_2) and nutrients (nitrate + nitrite designated as NO_3 , phosphate as PO_4 and silicate as $\text{Si}(\text{OH})_4$). The CTD salinity data were calibrated using salinity measurements of discrete samples (Autosal). In the 2000 and 2001 surveys, carried out onboard RV *Capricórnio*, temperature and salinity were measured with a Seabird CTD coupled to a Seabird rosette, equipped with Niskin bottles to collect the water samples. CTD salinity data were also calibrated.

O_2 was analyzed onboard following the Winkler method (Carrut and Carpenter, 1966)

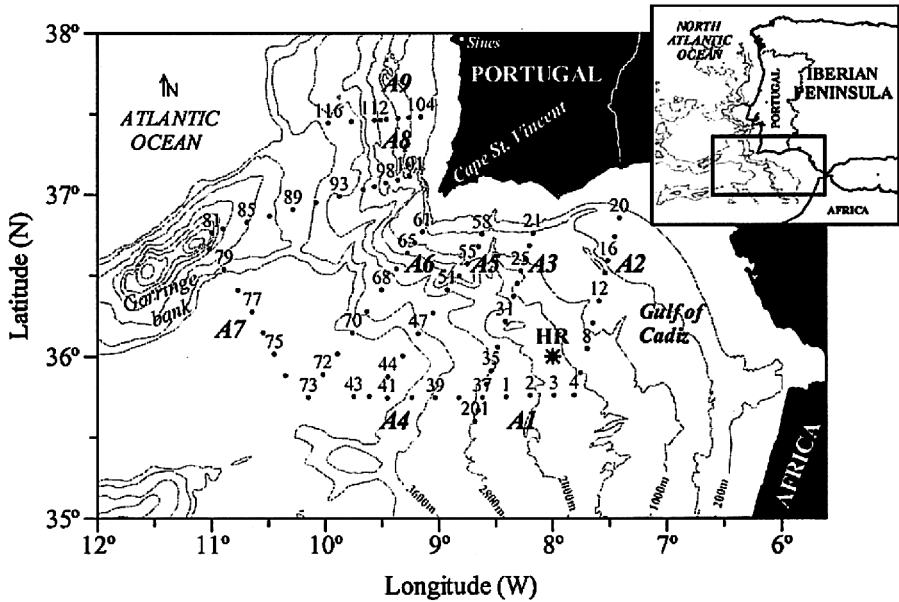


Figure 1. Map of the study area showing sections and position of sampling stations.

using a whole-bottle manual titration. The apparent oxygen utilization (AOU) was calculated as $\text{AOU} = \text{O}_{2\text{sat}} - \text{O}_2$ (O_2 is dissolved oxygen concentration and $\text{O}_{2\text{sat}}$ is saturation oxygen concentration in equilibrium with the atmosphere). Samples for determination of nutrients were poured into acid washed polyethylene cups and deep frozen onboard. Analyses were performed in the laboratory within two weeks, using a TrAacs Autoanalyzer. The preformed nutrients NO_3^0 and PO_4^0 (Broecker and Peng, 1982) were calculated using the stoichiometric ratios given by Ríos *et al.* (1989).

The potential density anomaly is expressed as γ_0 when referred to a sea pressure of zero dbar and γ_1 when referred to a sea pressure of 1000 dbar.

b. Data quality

Nutrient data quality was controlled through the continuous use of Sagami CSK Standards (Ambe, 1978). The IPIMAR laboratory also participated in the QUASIMEME exercises with satisfactory results. Precisions estimated by replicate analysis ($n = 10$) are the following: 1.1% for NO_3 (concentrations $15.0 \mu\text{mol/l}$), 1.3% for PO_4 ($0.5 \mu\text{mol/l}$) and 0.8% for $\text{Si}(\text{OH})_4$ ($5.0 \mu\text{mol/l}$). Intercalibrations of O_2 were carried out under the scope of two EU projects.

c. Water mass analysis

Water masses are described using potential temperature (θ), salinity (S), O_2 , AOU, NO_3 , PO_4 and $\text{Si}(\text{OH})_4$. The analysis is mainly based on (1) profiles of properties versus depth

and diagrams of Broecker's parameters versus salinity, from the isolated station; (2) plots of measured and preformed nutrients, and O_2 versus salinity from all the stations over the area of study; and (3) horizontal and vertical distributions of the selected limits of specific parameters along the boundary sections of the study area.

3. Results

a. Vertical high-resolution data

i. *Depth profiles.* An example of a layered structure present at intermediate depths (station HR) is shown in Figure 2. Salinity profiles in both sampling periods exhibit a clear subsurface salinity minimum (35.60–35.62) at 550 m depth below the permanent thermocline, corresponding to a characteristic potential density of 27.20–27.22 kg/m³. Beneath this depth, irregularities of thermohaline properties are depicted down to 800 m in July 2000 and 1200 m in October 2001. A sharp deeper minimum of salinity and temperature was detected in July 2000 at ~750 m while minima of these variables were present in October 2001 at depths ~800–900 m and also 1080 m. Between these minima slight increases in salinity and temperature were detected, whereas below the deepest salinity minimum a steady increase in salinity occurred down to 1160 m, attaining values as high as 36.20 in October 2001. Below this depth a sharp decrease in salinity and temperature is noticed.

Chemical properties associated with these thermohaline profiles are also shown in Figure 2 and data ranges corresponding to the extreme salinity values are presented in Table 1.

It is noticeable that the ranges of nutrients and AOU associated with the different salinity minima differ greatly. The lowest values of AOU, NO_3 , PO_4 and $Si(OH)_4$ correspond to the shallow well-defined salinity minimum layer, and the highest concentrations are associated with the deep salinity minimum. The existence of the minimum salinity water layers located between 750–1000 m is consistent with the presence in the study area of remains of the AAIW water type, as a recent work by Cabeçadas *et al.* (2002) revealed. At depths where the salty water is entrained a dilution of nutrients is observed, particularly below the deep salinity minimum, reflecting the presence of the oligotrophic MW main core. However, the MW water extending between the fresher water masses, when it mixes with the nutrient-enriched AAIW, gives rise to small increments of nutrients. The same water types were distinguished in both of the July 2000 and October 2001 occasions, although in this last sampling period below the MW main core, the fresher water mass North Atlantic Deep Water (NADW) was also detected through a nutrient enrichment.

ii. *Conservative properties.* The quasi-conservative parameters NO_3^0 and PO_4^0 are used to distinguish the water types and to give an indication of their mixing. The NO_3^0 -S, NO_3 -S, O_2 -S, PO_4^0 -S and PO_4 -S diagrams relative to data obtained at station HR in July 2000 are shown in Figure 3. Data collected from the surface down to 200 m were excluded. The

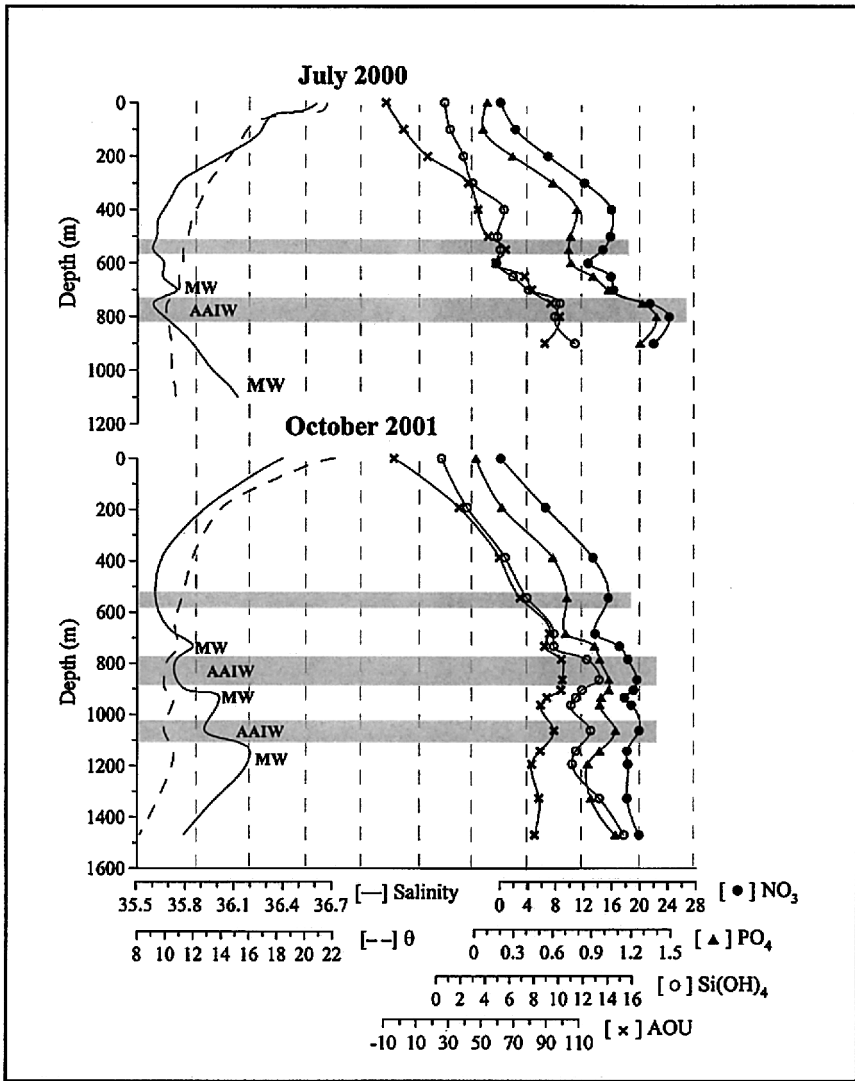


Figure 2. Vertical profiles of salinity, θ ($^{\circ}\text{C}$), NO_3 ($\mu\text{mol}/\text{kg}$), PO_4 ($\mu\text{mol}/\text{kg}$), $\text{Si}(\text{OH})_4$ ($\mu\text{mol}/\text{kg}$) and AOU ($\mu\text{mol}/\text{kg}$) at station HR in July 2000 and October 2001. Shaded area refers to minimum salinity intermediate water masses.

mixing of four water types seems to occur: the deepest layer of North Atlantic Central Water (NACW), corresponding to NO_3^0 values up to $11.1 \mu\text{mol}/\text{kg}$ and PO_4^0 up to $0.49 \mu\text{mol}/\text{kg}$, mixes with the shallow salinity minimum water layer that clearly exhibits lower nutrients ($\text{NO}_3^0 = 8.2 \mu\text{mol}/\text{kg}$ and $\text{PO}_4^0 = 0.32 \mu\text{mol}/\text{kg}$). Also, the AAIW that simultaneously exhibits the highest nutrients ($\text{NO}_3^0 = 14.4 \mu\text{mol}/\text{kg}$; $\text{PO}_4^0 = 0.79 \mu\text{mol}/\text{kg}$)

Table 1. Values of θ , AOU, NO_3 , PO_4 and $\text{Si}(\text{OH})_4$ at the salinity extremes, in July 2000 and October 2001 (station HR).

	Salinity	θ °C	AOU $\mu\text{mol/kg}$	NO_3 $\mu\text{mol/kg}$	PO_4 $\mu\text{mol/kg}$	$\text{Si}(\text{OH})_4$ $\mu\text{mol/kg}$
Salinity minimum at 550 m	35.60–35.62	11.30	65–74	14.7–15.5	0.7–0.72	5.2–7.4
Salinity minima at 750–1000 m	35.61–35.92	10.34–10.955	98–100	18.3–24.2	0.96–1.39	9.7–13.3
Salinity maximum at 1160 m (only in 2001)	36.20	10.80	86	18.2	0.96	11.4

and the lowest O_2 values ($175 \mu\text{mol/kg}$) is clearly visible. Entrainments of saline and slightly more oxygenated MW are noticed between the shallow salinity minimum water type and the AAIW and consistently below the latter.

The persistence of features, in terms of distributions of measured and preformed nutrients versus salinity (Fig. 3), indicates that mineralization is very unlikely to occur locally when mixing takes place.

b. Property-property plots over the entire study area

i. Temperature, AOU and nutrients versus salinity. Diagrams were constructed including all data obtained over the study area (Fig. 4) within the potential density anomaly interval $27.20 \leq \gamma_\theta, \gamma_1 \leq 32.35 \text{ kg/m}^3$. The upper limit corresponds to the water mass displaying the shallow salinity minimum, and the lower limit corresponds to the deeper part of the MW lower core. This core was defined by Ambar *et al.* (2002) as lying between $\gamma_1 = 32.00 \text{ kg/m}^3$ and $\gamma_1 = 32.35 \text{ kg/m}^3$ in the area considered.

The diagram of θ -S shows that intermediate waters lie in the range of salinity 35.58–36.71 and temperature 9.90–13.87°C (Figs. 4). The NO_3 -S, PO_4 -S and AOU-S patterns are dominated by an essentially unique salinity minimum of about 35.6 displaying a wide range of nutrients (NO_3 between 10.3 and 24.2 $\mu\text{mol/kg}$, PO_4 between 0.42 and 1.39 $\mu\text{mol/kg}$) and AOU (between 40 and 100 $\mu\text{mol/kg}$). This large variation is likely due to the presence of fresher water masses from different origins. As AAIW is oxygen-impoverished and often exhibits AOU values above 100 $\mu\text{mol/kg}$ (Kawase and Sarmiento, 1986), it was assumed that data points showing higher AOU values ($>80 \mu\text{mol/kg}$) in the salinity range 35.58–35.64 correspond to the modified water mass AAIW reaching the study area. Therefore, evidence emerges that most of the salinity minimum data points belong to a ventilated water mass.

The water layers exhibiting the highest salinities (36.50 to 36.71) display nutrients and AOU levels (Fig. 4) in the following ranges: NO_3 from 6.2 to 14.5 $\mu\text{mol/kg}$, PO_4 from 0.35

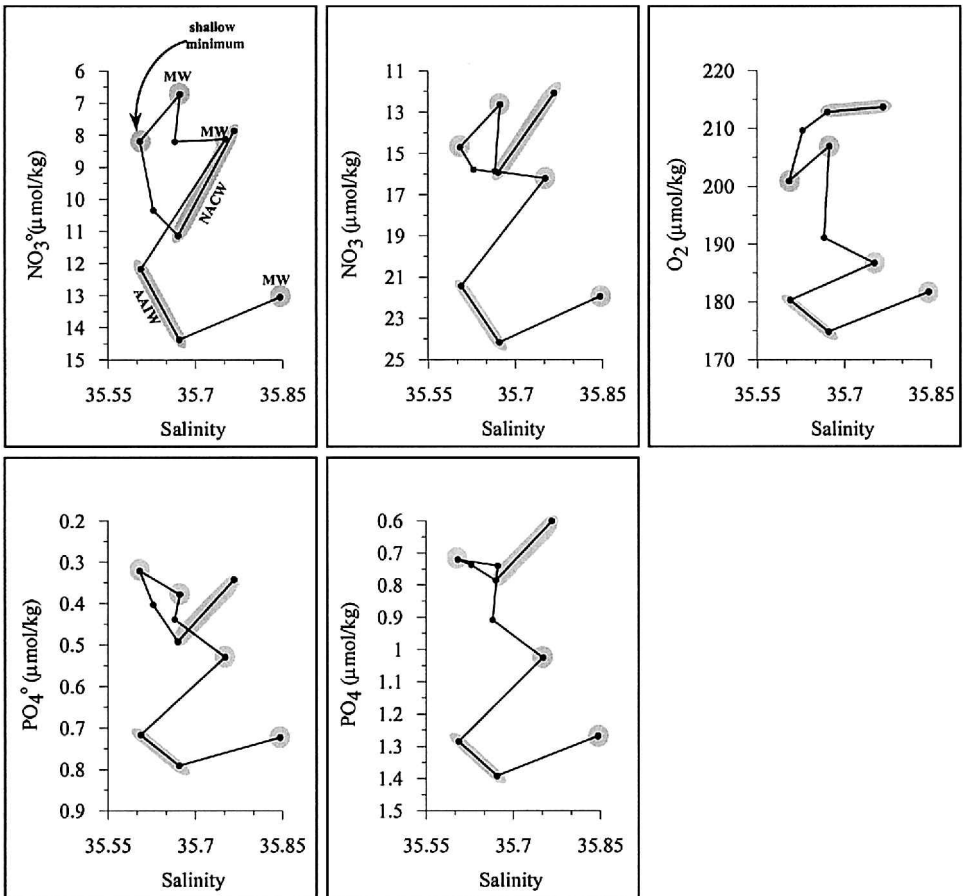


Figure 3. Nutrients (preformed and measured) and O₂ versus salinity at station HR in July 2000.

to 0.89 µmol/kg and AOU from 33 to 76 µmol/kg, as expected for the Mediterranean Sea Water (Minas *et al.*, 1991; Ambar *et al.*, 2002).

ii. Mixing triangle method. By analyzing diagrams of preformed nutrients and O₂ versus salinity, an attempt was made to clarify the origin and mixing processes of the intermediate water masses in the area under study. Mixing lines were chosen in order to envelop all data set points. It is observed in NO₃⁰-S and PO₄⁰-S diagrams (Fig. 5a, b) that a triangle is defined by mixing lines linking the Eastern Sill Water from Mediterranean (ESW) (sal = 38.45, NO₃⁰ = 2.3 µmol/kg and PO₄⁰ = 0 µmol/kg, calculated from Minas *et al.*, 1991 and Coste *et al.*, 1988), the nutrient-impooverished water from the Mediterranean outflow near Gibraltar (MWO) (sal = 37.37, NO₃⁰ = 1.0 µmol/kg and PO₄⁰ = 0 µmol/kg, estimated from Cabeçadas *et al.*, 2002) and the pure AAIW (sal = 34.3, NO₃⁰ = 20 µmol/kg from

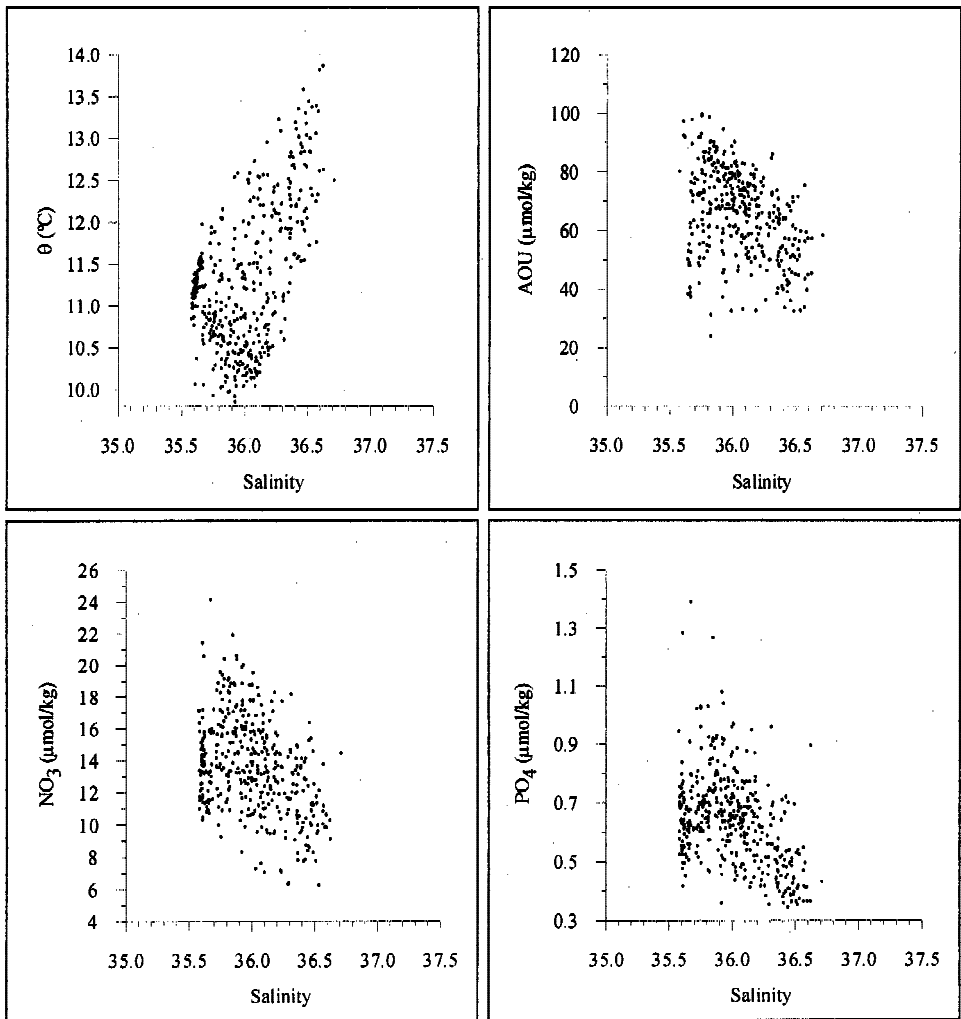


Figure 4. θ , AOU, NO_3 and PO_4 versus salinity for all sampling stations. Only data points in the potential density anomaly interval $27.20 \leq \gamma_\theta, \gamma_1 \leq 32.35 \text{ kg/m}^3$ are included.

Broecker, 1974 and $\text{sal} = 34.6$, $\text{PO}_4^0 = 1.4 \mu\text{mol/kg}$ from Broecker *et al.*, 1985). In order to enclose most of our data set points, besides the mixing line connecting water from the Mediterranean Outflow (MWO) and the pure AAIW, a further water mass end-member different from the ENACW is required, as the characteristics of ENACW ($\text{sal} = 35.81$, $\text{NO}_3^0 = 3.5 \mu\text{mol/kg}$ and $\text{PO}_4^0 = 0.19 \mu\text{mol/kg}$, Pérez *et al.*, 1993) are not appropriate. Such an end-member, likely responsible for the lowest nutrient concentration at the salinity minimum in our data set, may belong to the fresher water mass SAIW from northern origin. As a matter of fact, in O_2 -S diagram (Fig. 5c) the triangle defined by the ESW ($\text{sal} = 38.45$,

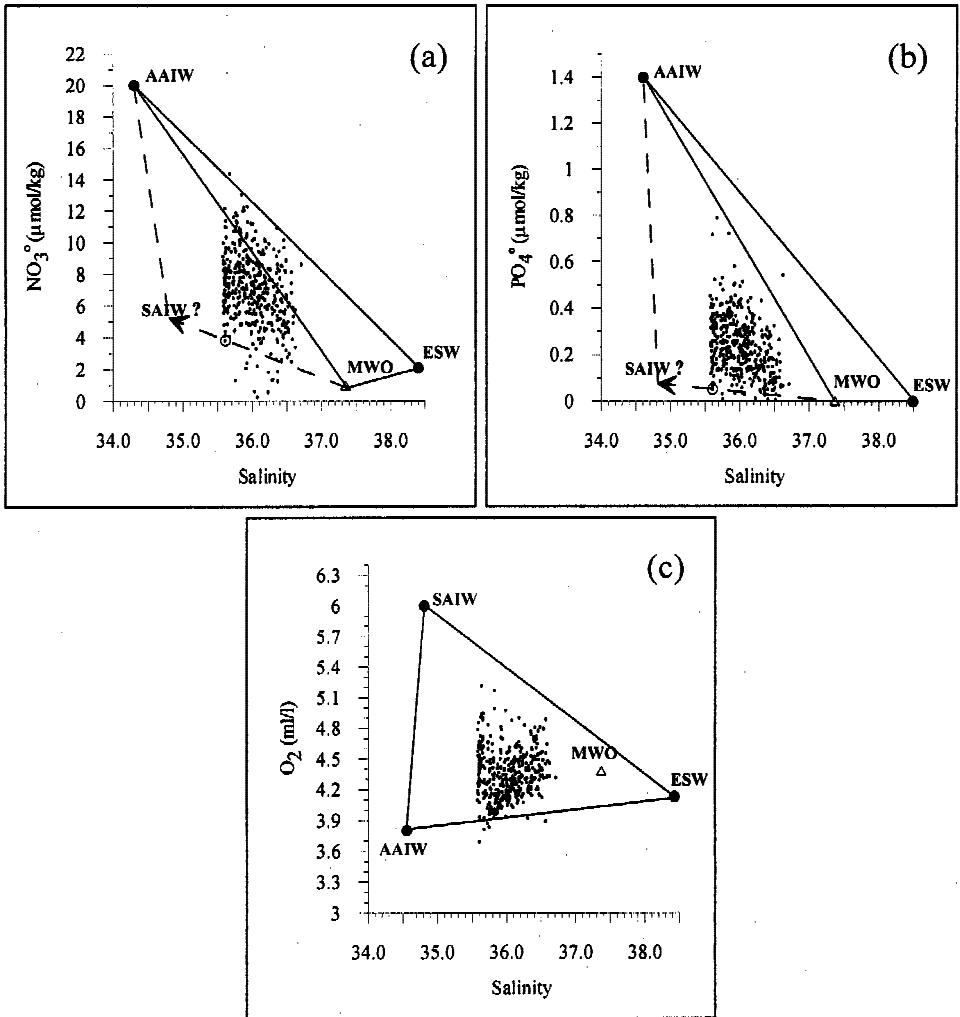


Figure 5. (a) NO_3^- -S (b) PO_4^- -S and (c) O_2 -S in the potential density anomaly interval defined in Figure 4.

$\text{O}_2 = 4.1$ ml/l from Minas *et al.*, 1991), the pure AAIW (sal = 34.55, $\text{O}_2 = 3.8$ ml/l from Hinrichsen and Tomczak, 1993) and the northern fresher water mass SAIW (sal = 34.80, $\text{O}_2 = 6.0$ ml/l, Harvey and Arhan, 1988) envelops most of our data, which points out SAIW that is an influent end-member in the area of study.

The few data points not enveloped by the O_2 -S diagram (Fig. 5c) corresponding to poorly oxygenated waters might be a consequence of mineralization processes taking place when the AAIW extends northward along the African margin (Kawase and Sarmiento, 1986; Harvey and Arhan, 1988). The lower concentration outliers visible in NO_3^- -S and

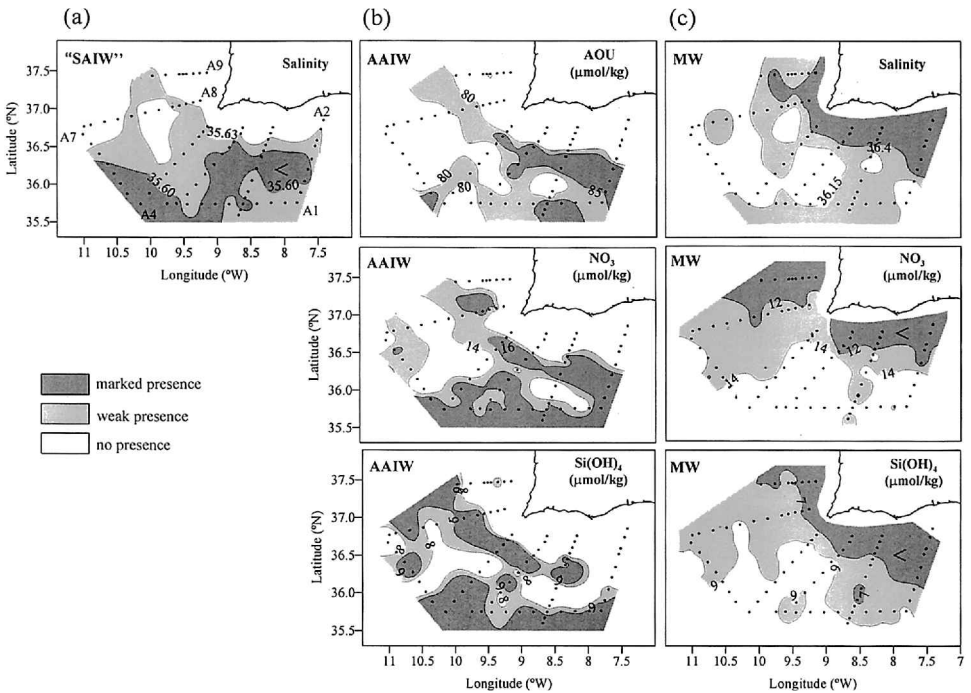


Figure 6. Horizontal contours of selected limits of (a) salinity for “SAIW” between 400–600 m (b) AOU, NO_3 , $\text{Si}(\text{OH})_4$ for AAIW between 600–1200 m and (c) salinity, NO_3 and $\text{Si}(\text{OH})_4$ for MW between 500–1600 m.

PO_4^{0-5} diagrams (Fig. 5a, b) correspond to sampling points located nearshore at the vicinity of Cape St. Vincent and canyons of Portimão and St. Vincent. This suggests that mixing near these sloping boundaries may have occurred, driving a downwelling-favorable circulation (Garrett, 1991) and causing nutrient dilution from shallow nutrient-impovertished depths.

c. Spreading of water masses at mid-depths

In order to follow the pathways of the intermediate water masses present in the area, and on the basis of their contrasting characteristics, limits for some properties were established.

Horizontal distributions of specific properties are shown in Figure 6. It can be observed that the water mass corresponding to the shallow salinity minimum (≤ 35.63), the modified SAIW lying between approx. 400 and 600 m (Fig. 6a), reaches the study area extensively and intrudes essentially from the south/southwestern boundary, being less noticed inshore and on the north/northwestern boundary of the region (transects A9 and A8). The modified AAIW (600–1200 m) displaying high AOU ($> 80 \mu\text{mol/kg}$) and high nutrient levels ($\text{NO}_3 > 14.0 \mu\text{mol/kg}$, $\text{Si}(\text{OH})_4 > 8 \mu\text{mol/kg}$) (Fig. 6b) is observed to penetrate the area of

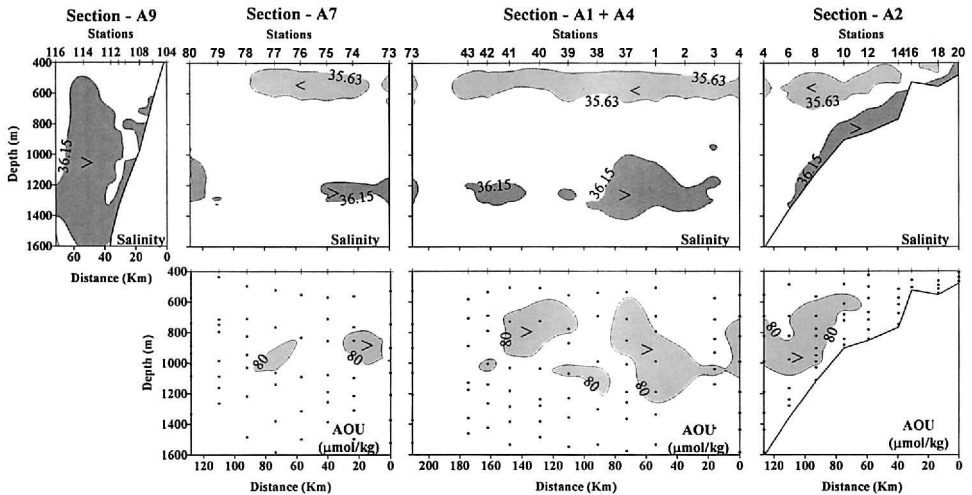


Figure 7. Vertical contours of salinity (for “SAIW” and MW) and AOU (for AAIW) along the boundary Sections A9, A7, A1 + A4 and A2.

study mostly through the south/southeast. Nevertheless, remnants of this water mass are still noticed off the western coast.

The more saline MW (sal > 36.4) (Fig. 6c) is depicted mainly nearshore along the southern coast and its distribution is clearly reflected in the pattern of nutrients, particularly NO_3 ($< 12 \mu\text{mol/kg}$) and $\text{Si}(\text{OH})_4$ ($< 4 \mu\text{mol/kg}$). However, its influence (sal > 36.15 , $\text{NO}_3 < 14.0 \mu\text{mol/kg}$, $\text{Si}(\text{OH})_4 < 9 \mu\text{mol/kg}$) is visible over practically the entire area of study. Actually, an increase of nutrients is observed in the MW outflow when the AAIW is directly overlying it. This pattern is also evident in other surveys carried out in the area (Cabeçadas et al., 2002).

The information provided through these horizontal distributions is complemented by the vertical patterns of selected limits for the “SAIW,” MW and AAIW characterization (salinity for “SAIW” and MW, and AOU for AAIW) at the boundaries of the area of study, as displayed in Figure 7.

Off the western coast, at section A9, the northern MW branch (sal > 36.15) occupies water depths from ~ 500 down to 1600 m, with no clear noticeable signature of fresher water masses, showing a less pronounced influence of “SAIW” and AAIW in that zone. Along section A7 remnants of the SAIW (sal < 35.63) are observed occupying the water column from ~ 400 to 600 m, and only a slight intrusion of AAIW (AOU $> 80 \mu\text{mol/kg}$) is revealed at approx. 800–1000 m, though the influence of the MW outflow (sal > 36.15) is well visible in this section, located nearby Gorrige Bank. In the southern section, A1 + A4 the presence of the shallow salinity minimum (< 35.63) attributed to the “SAIW” is detected in a continuous way. The AAIW through its high AOU signature at approx. depths 600–1200 m, is also irregularly revealed in this section, right above the MW saline lower

core. At section A2, the one nearest the Gibraltar sill, both fresh water masses (“SAIW” and AAIW) and the saline MW show a rise essentially due to slope effects. In fact, close to the shore (stations 20, 18, 16, 14 and 12) the “SAIW” is present at ~ 400 m and the MW at ~ 600 m, extending downwards to the bottom. The AAIW ($\text{AOU} > 80 \mu\text{mol/kg}$) lies from 600 to 1100 m depth between the “SAIW” and the MW and does not reach the inshore region. Actually, the three water masses are squeezed against the continental slope occupying up to 850 m in this region.

4. Discussion

The Mediterranean water current flowing westwards into the Atlantic strongly influences the hydrological and chemical properties of the fresher water masses that reach our study area. Some studies show that a stratified fresh water mass formed in the northwestern Atlantic, the SAIW, does enter the far-east North Atlantic (Harvey, 1982; Arhan *et al.*, 1994) although its transport eastwards of 20W is regulated by uncertain mechanisms (Wade *et al.*, 1997). Our results indicate that, as the high salinity MW and low salinity waters are encountered alternately, a confined region is formed displaying conditions favorable to the collapse of the fresher waters into a narrow range of salinity values 35.58–35.64. Therefore, the salty and warm MW present in the same density range as the fresher waters, functions to a certain extent, as a constraint to the penetration of these intermediate waters into the study region. The use of biogeochemical tracers made it possible to individualize the intermediate waters present. Specifically, the subsurface minimum salinity layer that lies practically everywhere over the area appears to be, on the basis of its chemical properties, a remnant of the SAIW. According to Read and Ellett (1991) this well-ventilated water mass showing AOI values of approximately $60 \mu\text{mol/kg}$ was detected between 49–54N, 20W centered at approx. 60 m depth. Also, Van Aken (2000) noticed a subsurface salinity minimum of 35.60 in a narrow zone near the continental slope off western Portugal, at pressures less than 450 db. On the other hand, he suggests that a subsurface salinity minimum observed west of the Iberian Peninsula represents a water mass that seems to derive from the Porcupine Sea Bight and northern Bay of Biscay. Further, he states that these water masses are characterized by relatively low AOI and nutrient values.

The deeper salinity minimum core found along the south of Portugal toward the Gulf of Cadiz has already been identified in the area as a branch of the AAIW (Cabeçadas *et al.*, 2002), although it was not clear whether it was coming from either the western North Atlantic or along the north-western African coast. Also, van Aken (2000) mentions a salinity minimum along the northwest African ocean margin at ~ 900 m depth, characterized by the highest AOI values ($> 100 \mu\text{mol/kg}$), which was consistent with its AAIW origin. Our results provide evidence that the AAIW present in the study area derives from the western African coast, a region that is known to be subjected to upwelling conditions that favor mineralization of organic matter, a process responsible for the enhancement of the AAIW chemical signature (Kawase and Sarmiento, 1986).

Finally, the saline MW outflow, markedly present in the entire study area, is observed to travel northward along the Iberian margin, as referred in other investigations conducted off the Portuguese continental slope (e.g. Zenk and Armi, 1990; Rhein and Hinrichsen, 1993). Further, information obtained in this restricted area indicates that the admixture of the MW outflow with the fresher intermediate water masses (“SAIW” and AAIW) is likely favorable to the formation of the several MW cores that display differentiated chemical properties, depending on the respective surrounding waters.

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