

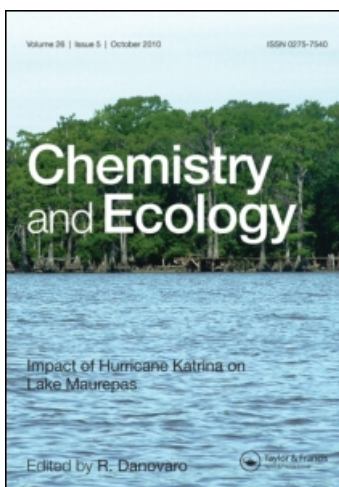
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## Multiparametric mixing analysis of the deep waters in the Western Mediterranean Sea

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The winters 2004/2005 and 2005/2006 were characterised by the formation in the north-western Mediterranean Sea of dense waters, which were significantly warmer and saltier than previously. The temperature-salinity diagrams show the presence of three different deep water types, a resident one and two newly formed ones. In order to quantitatively evaluate the filling of the deep Western Mediterranean Sea with these three different water masses from their formation region, an extended optimum multiparametric analysis (eOMP) has been performed, which permitted the estimation of the mixing fractions of the deep water masses in the area. The paper presents a comparison between the distributions of the three deep water types in 2005 and in 2006, in order to assess the spreading of the newly formed waters from their formation region.

**Keywords:** Multiparametric analysis; nutrients; deep water spreading; Western Mediterranean

### 1. Introduction

The knowledge of exact mixing fractions of water masses in the ocean is useful for various applications, especially in the analysis of transient tracer fields or biogeochemical cycling. The distribution of tracers is controlled by a combination of transport processes associated with the oceanic circulation and mixing and by reactive processes associated with the major biogeochemical cycles [1]. To evaluate the distribution of nutrients and tracers in the sea, the effects of mixing and of biogeochemical cycling must be resolved. The optimum multiparametric analysis (OMP hereafter) is a tool to analyse the water mass mixing in a water sample, by calculating the contributions of the original water masses (so called source water types, SWT hereafter) to the sample.

Tomczak and Large (1989, see [2]) formulated the OMP analysis after some improvements to the original multiparameter method [3] introduced by Mackas et al. (1987, see [4]). The OMP analysis is based on a simple linear mixing model. It assumes that all water mass properties undergo the

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same turbulent mixing process. Their distribution in space can therefore be determined through a set of linear mixing equations. The starting point of the OMP analysis is the observation of water mass parameters (such as temperature, salinity, oxygen etc). From these observations the OMP analysis tries to determine the contributions of predefined SWT, which represent the parameter values of the ‘unmixed’ source water masses. All data points to be analysed should therefore be located ‘downstream’ from the source water masses, in other words on the spreading path of the water masses. The SWT contributions or fractions for each data point are obtained by finding the best linear mixing combination in parameter spaces, defined by temperature, salinity, oxygen and nutrients, which minimises the residuals in a non-negative least squares sense [5]. The solution includes two physically realistic constraints: the contributions from all sources must add up to 100%, and all contributions have to be non-negative.

The OMP analysis can be performed in two different ways: the classical and the extended way. The classical OMP analysis (cOMP, see [2,3]) uses conservative or quasi-conservative parameters, which are not influenced by biogeochemical processes (i.e. temperature, salinity and dissolved oxygen). The extended OMP analysis (eOMP, see [6]) includes also dissolved inorganic nutrients as water mass tracers in the analysis, and takes the biogeochemical processes into account by introducing the Redfield ratios [7] into the equation system. In our case we have applied the extended OMP, because the higher number of variables (temperature, salinity, dissolved oxygen, nitrate, phosphate and silicate) permitted to resolve the mixing equation system for a higher (>2) number of source water types.

The analysis is applied to a data set which was collected in spring 2005 and in spring 2006, during two oceanographic surveys in a wide area of the Western Mediterranean (WMED), when hydrological and biogeochemical data were collected along nine transects (Figure 1). The distribution of physical properties, reported in the potential temperature – salinity ( $\theta$ -S) diagram (Figure 2a), evidenced a recent formation of a significant amount of new Western Mediterranean Deep Water (WMDW). The S-shaped structure has been observed in almost all investigated sub basins. The new WMDW has formed in the Gulf of Lions during winter 2004/2005 [8,9] and also

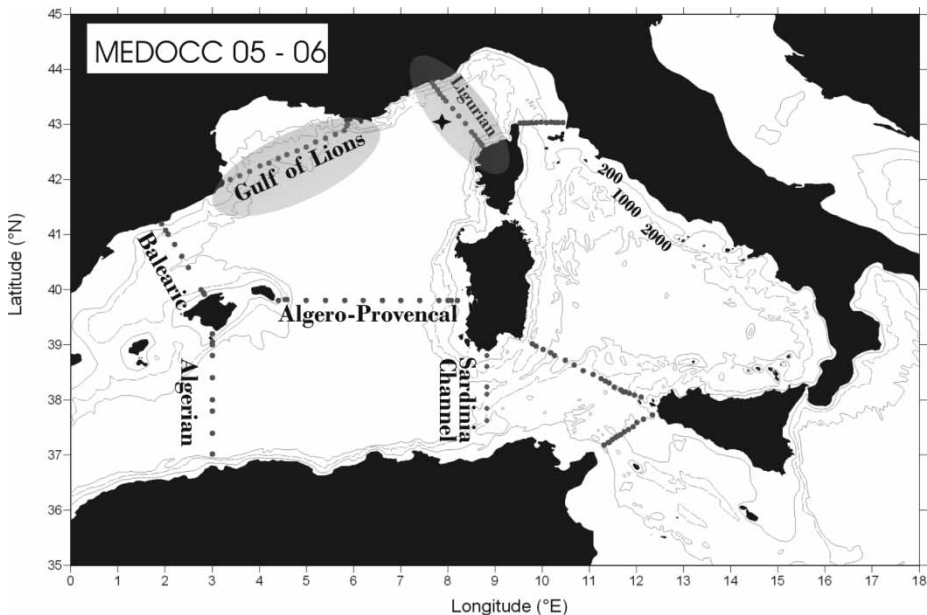


Figure 1. Station map of the two cruises. The shaded areas roughly correspond to the deep water formation region. The black star in the Ligurian Sea indicates the position of the DYFAMED station.

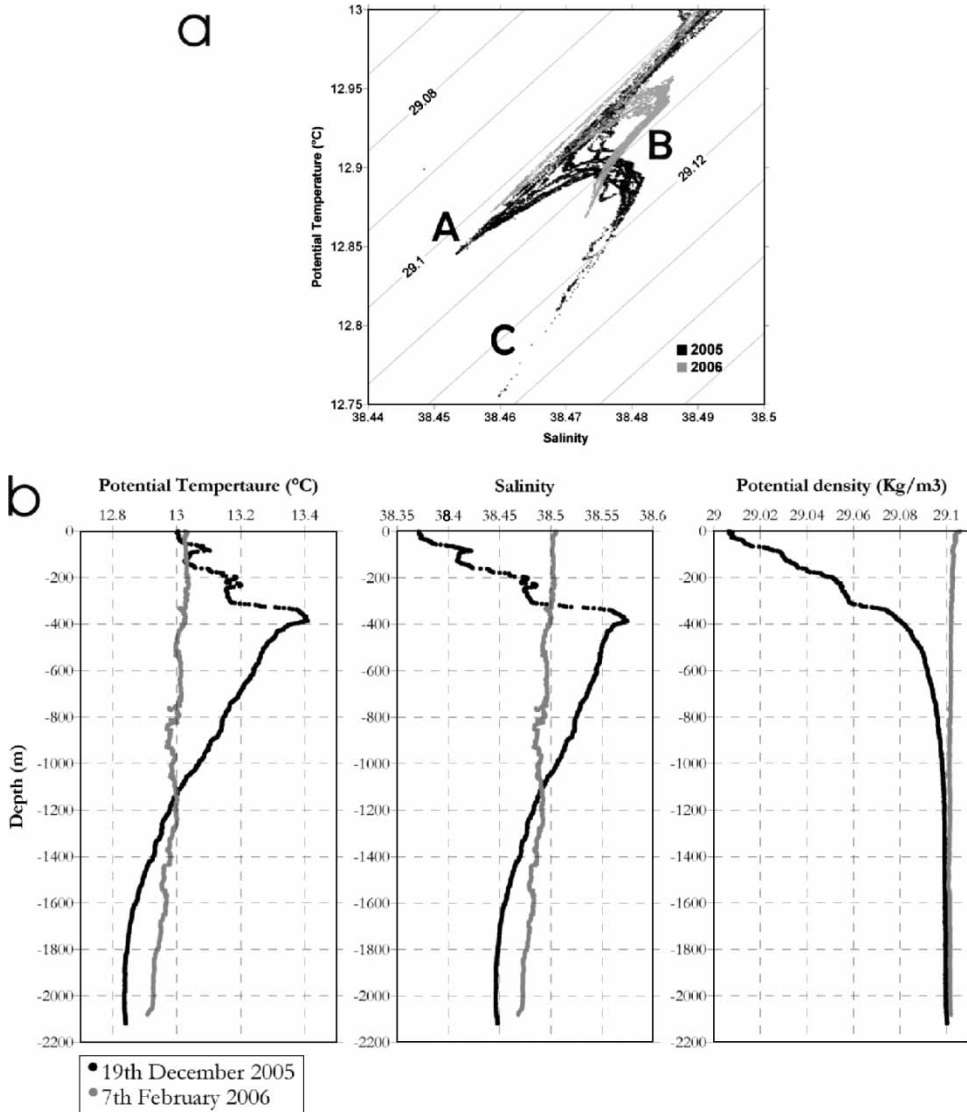


Figure 2. (a)  $\theta$ -S diagram of the deep layer in the Gulf of Lions in 2005 and in the Ligurian Sea in 2006; (b) vertical profiles of potential temperature, salinity and potential density at the DYFAMED station in December 2005 (black) and in February 2006 (grey).

during winter 2005/2006, when the DWF probably occurred mainly in the Ligurian subbasin. Looking at the  $\theta$  and S profiles in the Ligurian Sea (DYFAMED station) of 19 December 2005 and of 7 February 2006 (Figure 2b), the deep convection process is clearly evident: while in December 2005 a well-stratified water column was found, in February 2006 a completely uniform water column, from the surface to the bottom, is evident, with an almost constant potential density ( $\sigma_\theta$ ) value of  $29.103 \text{ kg m}^{-3}$ . Schroeder et al. (2006, see [9]) showed that the new WMDW was actually composed by three different water masses (types A, B and C, see their figure 2 of the cited manuscript). Water type A is the resident and older deep water, being characterised by a minimum in dissolved oxygen. Water type B and C are newly formed. In type B salinity and potential temperature show relative maxima together with dissolved oxygen concentration that

are higher than in type A. In water type C salinity and especially potential temperature drop down, while dissolved oxygen reaches a maximum.

As results clear from Figure 2a show, the same s-shaped deep structure was observed also in spring Figure 2a in the manuscript [9], the same S-shaped deep structure was observed also in spring 2006, even if with slightly different values of salinity and potential temperature. The still high dissolved oxygen concentrations suggest a strong formation event even in winter 2005/2006.

Deep anomalies in the WMED have been described by previous studies and [10] re-analysed data in the WMDW formation and spreading regions from 1971 to 2000. In this 30-year period they identified four events that have produced peculiar  $\theta$ -S characteristics in the deep layer, linking them to the cascading of dense water formation on the continental shelf, with a periodicity of about 8–11 years. The 2005 and 2006 anomalies have similar  $\theta$ -S shapes to those reported by [10], but the salt and heat contents are significantly higher. Recently [9] attributed the characteristics of the 2005 and 2006 anomalies not only to the interannual variability of the surface water on the continental shelf, but mainly to the progressive accumulation of salt and heat in the intermediate layer, as a consequence of the propagation of the signal of the Eastern Mediterranean Transient (EMT, see e.g. [11]) from the EMED (Eastern Mediterranean) to the WMED.

The aim of this study was to evaluate the mixing and to follow the spreading of the deep water masses in 2005 and 2006, by means of an extended OMP. The definition of our purpose went ahead from the observation that the newly formed deep water masses has been found even hundreds of kilometres away from their formation region.

## 2. Data and methodology

In spring 2005 and 2006 a wide area of the WMED was investigated. The oceanographic cruises MEDOCC 05 (from 24 April–16 May 2005) and MEDOCC 06 (8 June 2006–3 July 2006) were carried out by the CNR R/V *Urania* and provided an exhaustive upgrade of the hydrology of the whole basin. Figure 1 shows the CTD stations. The sampling points were chosen along 9 transects covering a wide area of the WMED.

At all the hydrological stations, pressure, salinity, potential temperature and dissolved oxygen concentration were measured with a CTD-rosette system consisting of a CTD SBE 911 plus and a General Oceanics rosette with 24 12-l Niskin Bottles. The CTD casts were performed from the surface to less than 10 m from the bottom. Temperature measurements were performed with a SBE-3/F thermometer with a resolution of  $10^{-3}$  °C and conductivity measurements were performed with a SBE-4 sensor with a resolution of  $3 \cdot 10^{-4}$  S/m. The probes were calibrated before and after the cruise at the NURC (NATO Undersea Research Centre) in La Spezia, Italy. Seawater samples for dissolved inorganic nutrients measurements were collected at different depths at 50% of all CTD casts, when the system CTD/rosette was going up. No filtration was employed, nutrient samples were stored at  $-20^{\circ}\text{C}$  and nitrate, orthosilicate and orthophosphate concentrations were determined later in the laboratory, using a Brän-Luebbe AutoAnalyzer following classical methods [12] with slight modifications. The data from the Service d'Observation DYFAMED (<http://www.obs-vlfr.fr/sodyf/home.htm>) at the DYFAMED site (black star in Figure 1) were used to observe the deep water formation event in 2005/2006.

## 3. Results and discussion

A critical task that arises from OMP mixing models is the definition of the source water masses. The actual parameter values for source water types can be found by reference to the literature or

Table 1. SWT properties as defined for 2005 and 2006 for the three water masses A, B and C. For each water mass two source water types are defined, that represent the 'unmixed' end-members (A1 and A2 for water mass A; B1 and B2 for water mass B; C1 and C2 for water mass C).

	A1	A2	B1	B2	C1	C2
2005 (Gulf of Lions)						
Potential temperature (°C)	12.855	12.945	12.875	12.904	12.757	12.872
Salinity	38.456	38.479	38.463	38.478	38.460	38.478
Oxygen ( $\mu\text{mol kg}^{-1}$ )	198	188	194	203	211	207
Phosphate ( $\mu\text{mol l}^{-1}$ )	0.368	0.455	0.437	0.338	0.368	0.425
Nitrate ( $\mu\text{mol l}^{-1}$ )	7.075	8.951	8.563	6.428	7.075	8.326
Silicate ( $\mu\text{mol l}^{-1}$ )	7.206	8.849	8.5092	6.639	7.206	8.301
Mass conservation	1	1	1	1	1	1
2006 (Ligurian Sea)						
Potential temperature (°C)	12.874	12.967	12.913	12.954	12.868	12.933
Salinity	38.459	38.482	38.472	38.486	38.473	38.484
Oxygen ( $\mu\text{mol kg}^{-1}$ )	187	180	189	190	196	192
Phosphate ( $\mu\text{mol l}^{-1}$ )	0.475	0.501	0.466	0.498	0.499	0.427
Nitrate ( $\mu\text{mol l}^{-1}$ )	8.75	10.08	8.61	9.37	8.93	7.05
Silicate ( $\mu\text{mol l}^{-1}$ )	7.27	10.17	7.12	9.25	8.05	5.96
Mass conservation	1	1	1	1	1	1

preferably by reference to observations from the water mass formation regions. Assuming that deep water formation events occurred both in winter 2004/2005 and in winter 2005/2006, the SWT were defined twice, using data collected in the formation region of the WMDW in 2005 (in the Gulf of Lions) and in 2006 (in the Ligurian Sea). The two definitions of the SWT are given in Table 1. To come up with these values we applied the procedure [4] of plotting all parameters against temperature for the data collected in the source region of the water masses, under the assumption that temperature is the main stratification parameter. The SWT definition relies on a linear approximation of the property-property relationships and has been determined by a best linear fit procedure. In order to include biogeochemical processes, the ratios between the non-conservative parameters (O2:P:N:Si = -150:1:21:19) have been computed from nutrient and oxygen data collected along the two sections used for the SWT definition (Gulf of Lions and Ligurian Sea). Some working hypothesis had to be assumed before applying the eOMP. Firstly we assumed that the deep water masses were formed in the north-western Mediterranean and secondly that they began their spreading path through the whole western Mediterranean Sea starting from this area. As reported by previous studies, in winter the north-western Mediterranean basin is the site of important dense water formation processes capable of triggering convective flows within the water column [13]. The processes are particularly intense in the Gulf of Lions [14], even though they have also been reported in the Balearic Sea [15] as well as in the central part of the Ligurian Basin [16]. Some inaccuracies occurred in our assumptions: (1) We initially supposed that the new deep water masses found in 2005 and in 2006 were formed in winter 2004/2005 and in winter 2005/2006, respectively. (2) The 'pure state' of water types A, B and C were defined by using the data collected in the Gulf of Lions and in the Ligurian Sea in spring (2005 and 2006), even if deep water formation processes took place in winter, since no winter data were available. (3) Previous studies [8,9] have shown that the new water types found in spring 2005 had actually formed in winter 2004/2005, while the new WMDW found in spring 2006 is probably a mixture of waters formed in winter 2004/2005 and in winter 2005/2006. Nevertheless, it was not possible to resolve the 2006 system for 5 water masses (old A, 2005-B, 2005-C, 2006-B and 2006-C), since not enough independent variables were available. The initial compromise was to consider that the new WMDW found in 2006 has originated only in winter 2005/2006 (experiment I). Afterwards a second experiment was carried out for the new WMDW found in

2006, using the SWT definitions of the previous year (experiment II) and the two solutions were compared.

In the following paragraphs the mixing percentages of the three deep water types and the mass residuals assessed for each solution are reported, with a final discussion on the spreading of the WMDW from its formation region.

### 3.1. Mixing fractions

The vertical distribution of mixing percentages for the three water types (A, B and C) observed in the four transects in 2005 and 2006 are shown in Figure 3. For a clear interpretation the orientation of the transects is briefly detailed: the Ligurian, the Balearic and the Algero-Provençal transects are shown with increasing longitude (the highest longitude on the right), while the meridional Algerian transect is represented with decreasing latitude, with the north on the left and the south on the right. The Ligurian Sea is by itself a dense water formation area, so the ‘new’ water found here could either have been advected from the Gulf of Lions or formed in situ. From the  $\theta$ - $S$  characteristics in this region (not shown) it was evident that the ABC structure was present in 2006, while in 2005 water mass C was completely absent (Figure 3a). In 2005 water type B occurred near the bottom mostly in the northern part of the transect, while water type A was present in almost the whole transect, with percentage higher than 80% above 2000 m depth (Figure 3a). In 2006 water type B was more abundant than in 2005 and water type C occurred in the bottom layer, while water type A was found only at depths shallower than in 2005 (Figure 3e).

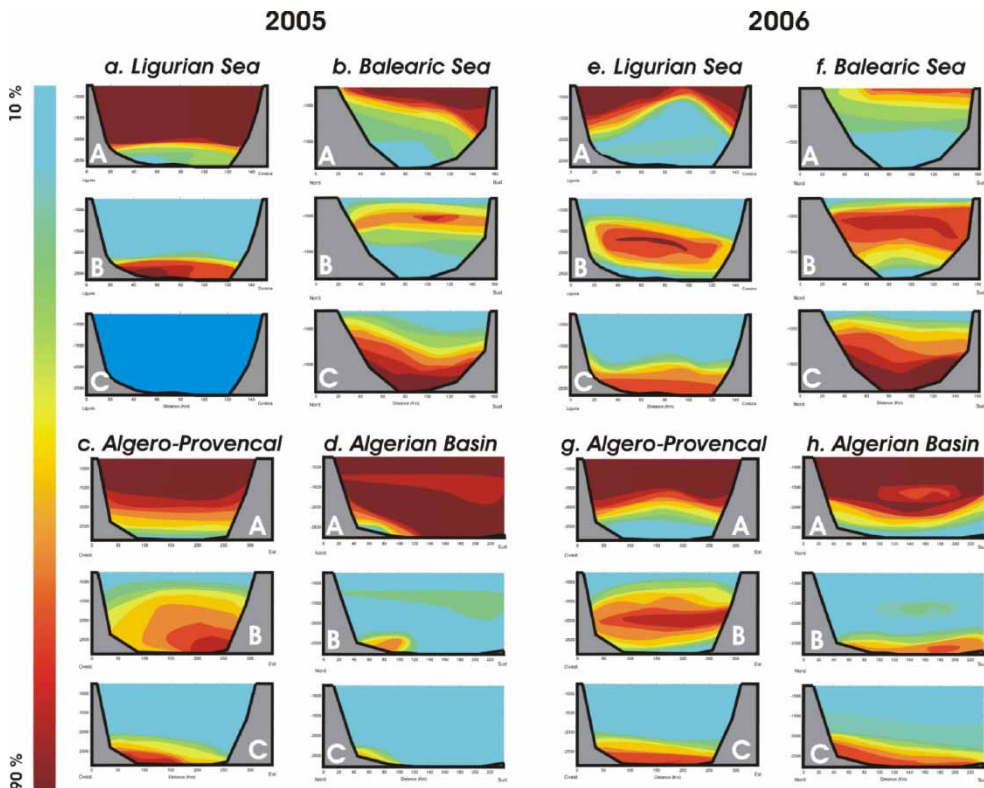


Figure 3. Mixing fractions of water masses A, B and C in 2005 and in 2006 between 750 m depth and the bottom: (a) and (e) Ligurian Sea; (b) and (f) Balearic Sea; (c) and (g) Algero-Provençal basin; (d) and (h) Algerian basin.

In the Balearic Sea, dense water formation events have been observed previously [15], so also in this case deep waters could have been advected from the Gulf of Lions or formed in situ. In 2005 the highest percentage of water type C were found in the northern part of the transect, with an overlaying layer of water type B, while the water type A was found above the newly formed types, with the highest percentages in the southern part of the transect (Figure 3b). Also here in 2006 we may note a major presence of the newly formed water types than in 2005, with water masses B and C occupying the whole layer below 1000 m depth and confining water mass A in a thinner layer shallower than 800 m (Figure 3f).

In the Algero-Provençal basin (Figure 3c), the newly formed water masses were advected from their formation area, since no deep water formation occurs in this area. The  $\theta$ -S diagrams (not shown) indicate a quite similar deep structure and an analogous spatial distribution. In 2005 the highest percentages of waters B and C were found in the eastern and in the western part of the transect, respectively. Water type A occurred in the whole transect above 1500 m (Figure 3c). In 2006, waters B and C occurred across the whole transect, while water A was uplifted by 200–300 m (Figure 3g).

In the Algerian basin the spatial extension of the new waters in the two years appear rather different, since in 2005 (Figure 3d) water types B and C were found with low percentage only in the northern part of the transect, while in 2006 (Figure 3h) they occupied the whole transect and water type A was not found in the bottom layer anymore.

The results of experiment II for the Algerian basin and the Algero-Provençal basin are shown in Figure 4. The main purpose of the two experiments was to consider to some extent that the deep layer of the southern transects are occupied by a mixture of water formed in winter 2004/2005 and those formed in winter 2005/2006. The mainly affected water mass seems to be water mass B, while the distributions of water masses A and C are quite similar for the two experiments. In particular, water mass B shows a more patched distribution, rather than a continuous layer

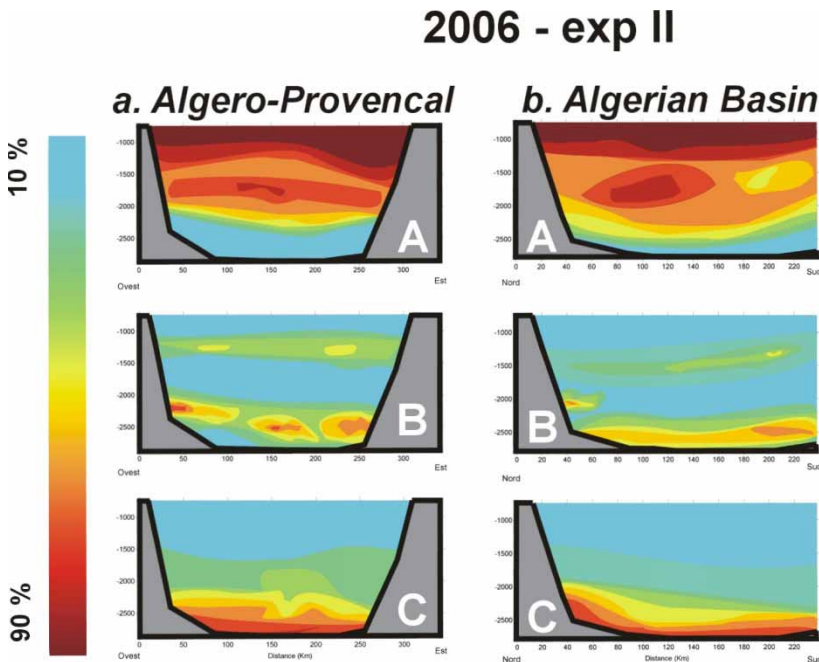


Figure 4. Mixing fractions of water masses A, B and C in 2006 between 750 m depth and the bottom in experiment II: (a) Algero-Provençal basin; (b) Algerian basin.



through the whole section. The sampling resolution was sufficiently high to state that these patches are real and not an interpolation effect. Probably this kind of distribution evidences the water formed during winter 2004/2005. Nevertheless, as we may observe from the  $\theta$  - S diagram in Figure 2a, the three water masses are quite similar in the two years and we have to remark that the mixing fractions in 2006 have to be interpreted as an indication on how the three water types are distributed along the transects, and are not necessarily related to a specific formation event.

No OMP was performed in the Sardinia Channel, since the characteristics are quite different in this region, because of the presence of deep water of Tyrrhenian origin. Nevertheless from the  $\theta$ -S data of 2006 (not shown) it was evident that water type B has been advected to the deepest (>2000 m) stations of the transect, very far away from its formation area, indicating that in 2006 the recently formed deep water has propagated to almost the entrance of the Tyrrhenian Sea.

### 3.2. Mass conservation residuals

In order to assess the goodness of the different solutions and to check the quality of the SWT definitions, an analysis of the distribution of the mass conservation residuals was carried out. For all solutions there is clearly a range, that roughly corresponds to the deep layer, where the analysis performs well, producing small mass residuals.

For the 2005 analysis, the mean residuals were always less than 10% in all observation points below 750 m depth in the four sections.

The ambiguity regarding the SWT definition for the 2006 observations can be partially solved by looking at the residuals of the two experiments. Far away from the formation area the new WMDW formed in winter 2004/2005 should be dominant with respect to the 2005/2006 formed one. In fact, comparing the residuals of experiment I and experiment II in the Algerian basin and in the Algero-Provençal basin, a clear reduction of mass residuals came out in experiment II, showing that probably the SWT definition has been improved in these two transects in experiment II. In both transects the new SWT definition produced residuals that on average were less than half the residuals of experiment I (6% vs 16%). In the Algerian transect more than 60% of the observation points below 750 m depth showed lower residuals in experiment II, if compared to experiment I. This percentage increases up to 80% in the Algero-Provençal transect. For completeness, experiment II was carried out also for the Ligurian Sea and in the Balearic Sea. In the former, the new water type definitions increased the magnitude of most residuals, while in the Balearic transect the magnitudes are very small and comparable for the two solutions.

### 3.3. Deep water spreading

In 2005 a newly formed deep water mass in the whole northern part of the investigated area was observed, in particular in the Gulf of Lions, the Ligurian Sea, the Balearic Sea and the Algero-Provençal basin, with a weak signature even in the northernmost part of the Algerian basin. Near Algeria the data indicate the 'normal' deep water structure. Following the OMP solutions and the respective mass residuals for each one, it seems that the deep water formed in winter 2005/2006 has pushed the older one away and so in 2006 a newer deep water in the northern part of the basin was observed, while the water formed in the previous winter has been observed in almost the whole southern part of the basin, reaching the entrance of the Tyrrhenian Sea. These results are confirmed also by an analysis of the vertical salinity, temperature and oxygen profiles in the single stations (not shown). But, since the OMP analysis did not permit to discriminate between different formation events (the number of SWT is too high), the main indication the analysis gives is the temporal evolution of the deep stratification along each transect, evidencing the relative displacements of the resident water type A and the denser new water types B and C.

The rapid spreading of the deep water masses, even far away from the formation area, e.g. towards the Algerian basin, may suggest that the new WMDW occupies almost the whole WMED: up to 2006 it seems that the only western basin which has not yet been reached by this deep features is the Tyrrhenian Sea.

#### 4. Conclusion

Deep water formation events in winter 2004/2005 and in winter 2005/2006 in the MEDOC area [13] have originated two different water types (B and C, see [9]). An eOMP analysis has been performed to assess the spreading and the spatial distribution of the three deep water masses in the WMED in spring 2005 and in spring 2006.

Two different experiments were carried out, in order to consider to some extent that the deep layer in the southern transects in 2006 is composed by a mixture between new water masses formed both in winter 2004/2005 and in winter 2005/2006. The results and a further analysis of the vertical property profiles in those areas corroborate the hypothesis that the deep water formed in winter 2005/2006 has pushed the older one southward, farther away from the formation region in the north-western Mediterranean Sea. Nevertheless, beyond this hypothesis, which could be only partially verified with the OMP, the analysis evidenced the evolution of the displacements of three different deep water masses along four transects in the WMED, between 2005 and 2006. The deep layer is occupied by an older deep water (type A), below which the newly formed water types are recognised. The mixing fractions along the transects in the whole basin indicate that generally in 2006 water type A was more marginal than in the previous year and the recently formed water types B and C were more abundant, even far away from the formation area. In particular, type C was found with higher percentages and in a wider region in 2006 than in 2005.

The data we collected in the western basin demonstrate that almost the whole deep WMED has filled up with these peculiar deep water masses, with the exception of the Tyrrhenian Sea. An outstanding question is about the eventual effect of these salty and warm deep waters, which filled the basin within 2 years, on the Mediterranean Outflow to the Atlantic, an issue that should be addressed in future surveys.

#### Acknowledgements

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