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In this study we estimate diffusive nutrient fluxes in the northern region of Cape Ghir upwelling system (Northwest Africa) during autumn 2010. The contribution of two co-existing vertical mixing processes (turbulence and salt fingers) is estimated through micro- and fine-structure scale observations. The boundary between coastal upwelling and open ocean waters becomes apparent when nitrate is used as a tracer. Below the mixed layer (56.15 ± 15.56 m), the water column is favorable to the occurrence of a salt finger regime. Vertical eddy diffusivity for salt ($K_s$) at the reference layer (57.86 ± 8.51 m, CI 95%) was $3 \times 10^{-2}$ ($1.89 \times 10^{-9}$, CI 95%) m² s⁻¹. Average diapycnal fluxes indicate that there was a deficit in phosphate supply to the surface layer ($6.61 \times 10^{-4}$ mmol m⁻² d⁻¹), while these fluxes were 0.09 and 0.03 mmol m⁻² d⁻¹ for nitrate and silicate, respectively. There is a need to conduct more studies to obtain accurate estimations of vertical eddy diffusivity and nutrient supply in complex transitional zones, like Cape Ghir. This will provide us with information about salt and nutrients exchange in onshore–offshore zones.

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1. Introduction

In the open ocean, cross-isopycnal mixing via turbulence is the main route of nutrients from the deep layers to the well-lit surface waters where they fuel phytoplankton primary productivity (Hamilton et al., 1989). These diapycnal turbulent fluxes also are especially important in coastal upwelling regions as the irreversible part of the physical mixing process (Hales et al., 2005). They act as a nutrient replenishment mechanism in the coastal shelf but also as a continuous nutrient transport through the water column to the surface (Hales et al., 2005). Although the magnitude of advective transport may surpass that of vertical turbulent diffusion by up to four orders of magnitude, it should be pointed out that the latter has a permanent and irreversible character at spatial and temporal scales (Hamilton et al., 1989; Hales et al., 2005).

Despite the relevance of vertical turbulent diffusion in mixing processes, the continuous application of inadequate local micro- and fine-structure parameterization schemes in field studies has often led to an inconsistency in biological uptake and nutrient supply estimates (Dietze et al., 2004). Such inaccurate estimates inevitably hinder our ability to constrain biological activity rates such as ‘new production’ and associated carbon export to the deep ocean (Dugdale and Goering, 1967; Hamilton et al., 1989; Oschlies, 2002). Turbulent vertical mixing includes processes which take place at fine-structure scale (1–10 m) and micro-structure scale (< 1 m) (Gargett, 1976; Gregg, 1989).

Quantifying the relationship between micro- and fine-structure is essential in order to establish connections between both scales when parameterizing the effects of these turbulent processes (Schmitt et al., 1988). On the other hand, given the resolution and sensitivity of Oceanic General Circulation Models (OGCMs) with respect to vertical turbulent diffusion it is of particular importance to deepen our knowledge on mixing processes at fine-structure scale (Large et al., 1994; Zhang et al., 1998; Law et al., 2003).

The prevailing vertical diffusive mixing mechanisms at central waters (majorly the Atlantic basin, Southeast Indian Ocean, and Southwest Pacific Ocean) are as follows: (1) the vertical shear (mechanical turbulence produced by horizontal currents), (2) salt fingers (double diffusion), and (3) internal waves (Hamilton et al., 1989; MacDougall and Ruddick, 1992; Figueroa, 1995). The contribution of (3) is usually low and varies according to the inner energy of the wave (Garret–Munk internal wave model), and...
according to a floatability constant (Garrett and Munk, 1972, 1975; Large et al., 1994). In general terms, internal waves are considered constant or are totally disregarded. The contribution of (1) and (2) is independent given their intermittent nature both in space and time (McDougall and Ruddick, 1992). Salt fingers occur in highly stratified systems where relatively warmer and saltier water lays over cooler and less saline water. The molecular diffusion of heat is faster than that of salt, which makes the more saline layer to become more dense forming convection plumes (termed ‘salt fingers’), which conserve its salinity variance. These structures move downwards efficiently mixing the water vertically (St. Laurent and Schmitt, 1999). Indeed, Hamilton et al. (1989) observed that previous measurements of vertical diffusive nitrate fluxes which only considered dissipation-diffusivity methods (Osborn, 1980; Gregg, 1989) were six times lower than diapycnal fluxes induced by salt fingers.

For this reason, in regions such as the subtropical Northeast Atlantic where central waters dominate (North Atlantic Central Water – NACW), and where the efficiency of salt finger mixing has been recognized, the use of combined parameterization models for salt vertical eddy diffusivity ($K_s$) is essential (Hamilton et al., 1989; McDougall and Ruddick, 1992; St. Laurent and Schmitt, 1999).

The northern boundary of Cape Ghir upwelling region is an important transition zone for cross-shelf exchange of biogenic materials and nutrients between the coast and the adjacent open ocean (Mason et al., 2012). This exchange occurs mainly through the recurrent upwelling filaments (Álvarez-Salgado et al., 2007), which are mesoscale features which may extend hundreds of kilometers offshore. The Cape Ghir coastal transition zone is also subject to strong seasonal variability mainly associated with the intensity of the coastal upwelling and the variability of the Canary Current (Barton et al., 1998; Pelegrí et al., 2005a, b).

The aim of this study was to estimate the magnitude of diapycnal fluxes of different nutrients in the northern boundary of the Cape Ghir region. The observations were carried out in the frame of the PROMECA project (Mixing Processes in the Canary Basin), during autumn 2010, when the trade wind regime is weak and the coastal upwelling is less intense (Barton et al., 1998). In addition, here we examine the relationship of $K_s$ at micro- and fine-structure scale. Finally, we estimate the relative contribution of the mixing processes involved (mechanical turbulence and salt fingers) and the diapycnal nutrient fluxes at fine-structure.

2. Data and methods

The data used in this study was collected during the PROMECA cruise onboard the R/V García del Cid from 18 to 29 October 2010. Fourteen hydrographic stations in the region north of Cape Ghir (Fig. 1). The horizontal resolution between stations was from ~5 to 60 km. Temperature and salinity measurements were obtained at 1 db intervals using a SBE 911 plus CTD probe mounted on a rosette sampler equipped with 12 Niskin bottles (12 L). Seawater samples for nutrient analysis were collected in 15 mL polyethylene tubes (WVR) at 50, 75, 100, 150, 200, 250, 350, 500, 800, 1200, 1500 and 2000 m depth. The samples were stored frozen at ~20°C until analysis ashore. Nutrient concentration analyses were performed using an AA3 Bran+Luebbe autoanalyzer with detection limits of 0.01, 0.001, 0.02 and 0.016 μM for nitrate, nitrite, phosphate and silicate, respectively. In this study, we will refer to ‘nitrate’ as nitrate plus nitrite.

Fine-structure scale measurements were obtained using the vessel-mounted Ocean Surveyor ADCP (SADCP) at 75 kHz (8 m cell size). Current velocity data was processed with the CODAS software (Common Ocean Data Access System; Firing et al., 1995). Measurements of turbulent kinetic energy dissipation rate ($\varepsilon$) and thermal variance ($\chi$) were performed using a vertical free-falling micro-structure profiler (TurboMAP) at integrate intervals of 2 m down to ~470 m depth. The TurboMAP was equipped with shear probe ($\Delta u/\Delta z$), temperature ($\Delta t/\Delta z$) and CTD probes. Free-falling speed was ~0.6–0.7 m s$^{-1}$ at a rate of 512 Hz. The data was processed using TMTools (version 3.04A) (TMTTools, 2008).

2.1. Micro- and fine-structures processing

Our study was focused on the depth comprised between below the mixed layer depth (MLD) and ~600 m. For this reason, a reference layer was established as the depth where the vertical transport of nutrients to the surface waters did not involve the mixed layer. This ensures the correct delimitation of the boundary layer oceanic mixing regime near the surface in order to apply the appropriate mixing schemes (Large et al., 1994). Finally, the reference layer at each station was established as the level of maximum Brunt–Väisälä frequency plus 10 m, which was in good agreement with the estimated MLD using the algorithm by Kara et al. (2000). SADCP and nutrient profiles were linearly interpolated at the same
vertical resolution (10 m) and depth. This interpolation does not increase de variance of the signal. Temperature and salinity data were smoothed using a weighted average filter at the same vertical resolution. Given the nature of the data used, this study aimed to conduct a brief micro- and fine-structures description to characterize the water column according to dissipation and stability parameters. Thereafter, we evaluated micro- and fine-structures in terms of $K_f$ in order to estimate nutrient fluxes at all hydrographic stations at fine-structure scale (10 m) (Fig. 1).

The latter, with the aim to optimize the number of the in situ measurements and get maximum spatial coherency and sinoplicity according to nutrient profiles. Eddy diffusivity for salt ($K_s$), nutrients) at each depth was calculated as the sum of turbulence ($K_{st}$) and salt fingers ($K_{sf}$) (McDougall and Ruddick, 1992; Hamilton et al., 1993; St. Laurent and Schmitt, 1999).

Since both processes are of turbulent nature, the mixing processes not related with the double diffusion ($K_d$) were defined as the diffusivity due to turbulent mixing ($K_{st}$) in this study. Following the weighing model of St. Laurent and Schmitt (1999) the contribution of both mixing processes to vertical eddy diffusivity was examined and calculated as $K_f = K_{st} + K_d$, where $P_l = 1 - P_f$ and $P$ correspond to the weighing factor. Discrimination between turbulence and salt fingers was established according to the mixing efficiency ($\Gamma_{obs}$) and density ratio ($R_f$) from Turner angle ($\Gamma_t = 70$–90 salt fingers; $-45 < \Gamma_t < 70$ turbulence) (McDougall and Ruddick, 1992; St. Laurent and Schmitt, 1999). Nutrient diffusive fluxes at fine-structure scale (10 m intervals) were finally calculated following Fick’s law ($\text{Flux} = -K_s \Delta u/\Delta z$), where $K_s = K_{st} + K_{sf}$, is the eddy diffusivity for the salt (nutrients) and $\Delta u/\Delta z$ are the nutrient gradients in the depth interval of interest (Csanyi, 1973).

2.1. Micro-structure

$K_s$ was calculated assuming that both turbulence and salt fingers follow the steady state turbulent kinetic energy (TKE) and thermal variance equations (McDougall and Ruddick, 1992; St. Laurent and Schmitt, 1999). Firstly, the dissipation rate was computed from the fluctuating component of horizontal velocity ($\varepsilon \approx (15/2)u_T^2 + v_T^2$) and thermal variance ($\langle \chi \approx 2kT \delta T^2 \rangle$), where $\nu$ is the molecular viscosity and $k$ is the thermal diffusivity. Turbulent mixing of salt was estimated following Osborn (1980) and Oakley (1988):

$$K_{st} = \Gamma_{obs} \frac{\varepsilon}{\nu^2} \tag{1}$$

where $\Gamma_{obs}$ is the mixing efficiency due to turbulence ($Osborn, 1980$; Hamilton et al., 1993) and $N^2$ is the Brunt–Väisälä frequency. The mixing efficiency observed associated with both processes $\Gamma_{obs} = N^2 \chi^2/2\varepsilon（R_f^2）$ was calculated in order to discern between turbulence and salt fingers $\varepsilon_f = (\Gamma_{obs} - \Gamma_{f})/\Gamma_{f}$ (Turner, 1973; Ruddick, 1983). As well as to estimate the dissipation rate $\Gamma_f = \varepsilon (R_f - 1)/R_f (1 - \gamma)$ and the flux ratio $\gamma = 1/(1 + ((R_f - 1)/R_f)^{1/2})$ due to salt fingers (Hamilton et al., 1989; McDougall and Ruddick, 1992; St. Laurent and Schmitt, 1999). The density ratio $R_f = d \Delta z_f / \Delta S_f^2$ is used to identify the double diffusion regime.

Thermal expansion ($\alpha$) and haline contraction ($\beta$) coefficients were calculated using MacDougall’s (1987) algorithms. Finally, salt eddy diffusivity due salt fingers was estimated following Hamilton et al. (1989) and McDougall and Ruddick (1992):

$$K_{sf} = \frac{R_f - 1}{\Gamma_f} \tag{2}$$

We assume that the thermal diffusivity $K_f = \chi/2(\theta_2)^2$ is not equivalent to salt and/or density in a salt finger regime, unlike pure turbulent environments (Osborn and Cox, 1972).

2.1.2. Fine-structure

Vertical eddy diffusivity for salt ($K_f$) was estimated following the parameterization of Zhang et al. (1998) (ZSH98). This scheme depends on $R_f$ and combines turbulence and double diffusion constituting an ad hoc relationship, which was established by Schmitt (1981) and validated by St. Laurent and Schmitt (1999) and Inoue et al. (2007). Eddy diffusivity for salt was calculated as follows ($K_{sf} = K_{st}$):

$$K_f = \frac{R_f \varepsilon_f \varepsilon_{st}}{\Gamma_f - 1} \tag{3}$$

Assuming that this equation is locally linear where $K_f = K_s = K^\infty$ and the diapycnal diffusivity rate is a constant representing mixing associated with internal waves. Although the turbulence associated with vertical shear can be included as a function of gradient Richardson number ($R_f$, e.g. Yu and Schopf, 1997; Pacanowski and Philander, 1981), in this case we chose not to modify the model by ZSH98 to allow comparison with previous studies. Salt eddy diffusivity in a salt finger favorable regime was calculated as follows:

$$K_f = \frac{K^\infty}{1 + (R_f K_s K_f)} + K^\infty \quad \tag{4}$$

where $K^\infty = 10^{-4}$ m$^2$ s$^{-1}$ is the maximum diapycnal diffusivity due to salt fingers; $K^\infty = 3 \times 10^{-5}$ m$^2$ s$^{-1}$ is the diapycnal diffusivity constant due to processes unrelated with double diffusion, like internal wave breaking; $R_f = 1.6$ is the density ratio ($R_f$) where the mixing due to the diapycnal salt fingers falls sharply due to the absence of staircases; $n = 6$ is an index to control the rate of $K_s$ decay with $R_f$ increase (Zhang et al., 1998).

In order to examine the instability of the water column due to current velocity, we additionally calculated the gradient Richardson number ($R_i = N^2 / \alpha^2$), where $\alpha^2 = (\Delta u/\Delta z)^2 + (\Delta v/\Delta z)^2$, $\alpha$ and $\nu$ are the horizontal components of current velocity at the same depth. The Turner angle ($\Gamma_t = \tan^{-1}(R_f + 1 / (R_f - 1))$ was used as an indicator to confirm the diffusive regime type according to the density ratio ($R_f$) (Turner, 1973; Ruddick, 1983).

3. Results and discussion

3.1. Micro- and fine-structures interpretation

The $T$–$S$ diagram for the 14 hydrographic stations sampled revealed the depth region of interest for this study (NACW between 26.4 and 27.3 isopycnals, Fig. 1). The mixed layer was located at $46.15 \pm 15.56$ m (± SD). Below the mixed layer, the reference layer oscillated between 30 and 80 m depth ($56.15 \pm 15.56$ m). This zone was dominated by the presence of the NACW (at ~600 m depth). Given the close $T$–$S$ relationship observed (Fig. 1), we can establish that turbulence (involving internal wave breaking and double diffusion) controls the mixing process (Schmitt, 1981; Ferrari and Polzin, 2005). Fig. 2 shows an average profile (stations 24 and 34–50) for each depth level, combining micro- ($\varepsilon, \chi$, Fig. 2a and b) and fine-structure ($R_f, R_i$, Fig. 2c and d) measurements. The highest micro-structure values were observed at 90–110 m (Fig. 2a and b), just below the ML depth range among stations (30–80 m).

Dissipation rates and thermal variance showed a high variability with depth (Fig. 2a and b). Averages were (e.g.) $4.31 (\pm 3.41) \times 10^{-9}$ m$^2$ s$^{-3}$ ($\varepsilon$) and $1.20 (\pm 0.81) \times 10^{-9}$ m$^2$ s$^{-3}$ ($\chi$) at CI 95% about 100 m depth. With respect to these values, the logarithmic distribution of a large number of micro-structure measurements obtained from the central waters of the Canary basin (26 N–28 W, NATRE site) reveals the presence of two dissipative modes (high and low) related to the two mixing mechanisms present (turbulence and
Furthermore, the mixing efficiency is the dominant dissipative process (St. Laurent and Schmitt, 1999). According to this bimodal distribution statistical model (NATRE site), ranges from $\sim 2 \times 10^{-10}$ to $7 \times 10^{-8}$ m$^2$ s$^{-3}$ (low mode, salt fingers) and $\sim 7 \times 10^{-9}$ to $2-3 \times 10^{-8}$ m$^2$ s$^{-3}$ (high mode, turbulence) were established (Ruddick et al., 1997; St. Laurent and Schmitt, 1999). St. Laurent and Schmitt (1999) established a thermal variance ($\chi$) rate threshold value to identify salt finger favorable regime of $\chi > \chi^2 \sim 1.0 \times 10^{-3}$ C$^2$ s$^{-1}$. Although the micro-structure measurements obtained in this study ($\varepsilon$ and $\chi$) are in the range of those found in the previous works (St. Laurent and Schmitt, 1999) it should be taken into account that these parameters have a large natural variability and that their statistical distribution requires including an elevated number of profiles, adding to a rigorous averaging method to obtain diffusivity estimations (Ruddick et al., 1997). However, considering that the mixing efficiency ($\Gamma_{\text{mix}}$) derived from the micro-structure is related to the stability parameters ($R_p$ and $Ri$) (St. Laurent and Schmitt, 1999) and for this particular case, the latter indicators can be more decisive in the characterization of mixing process in the water column. Average values of $R_p$ and $\log_{10}(Ri)$ were $-2.61 (\pm 8.57)$ and $0.59 (\pm 0.36)$ (CI 95%) at 100 m depth, respectively (Fig. 2c and d).

In this depth range, the negative values of $R_p$ indicate a stable double diffusion regime (absence of salt fingers and diffusive regime; Ruddick, 1983), which is in agreement with the mixed layer base mentioned above (Fig. 2a and b). Overall, the values of $Ri$ ( $> 1$) reveal a moderate instability system in this case, due to the weak shear observed (Fig. 2d). The system maintains an $R_p \pm 1.9$ below $\sim 130$ m depth, which indicates a favorable salt fingers regime (Ruddick, 1983). In salt finger favorable systems, both fingers and turbulence act as dissipative mechanisms (St. Laurent and Schmitt, 1999). In contrast, in a doubly stable regime (e.g. with negative values of $R_p$ at mixed layer, Fig. 2c), turbulence is the dominant dissipative process (St. Laurent and Schmitt, 1999). Furthermore, the mixing efficiency observed ($\Gamma_{\text{mix}}$) indicates the coexistence of both mixing processes in accordance with the ranges previously established in laboratory experiments and oceanographic field applications (Fig. 3; Osborn, 1980; Hamilton et al., 1989; McDougall and Ruddick, 1992; Hamilton et al., 1993; Ruddick et al., 1997; St. Laurent and Schmitt, 1999). The flux ratio ($\gamma$) (Fig. 3) shows a range of $0.4 < \gamma < 0.7$, being the majority of the observations between 0.5 and 0.7, which is also consistent with the salt finger models derived from laboratory experiments and that usually found in the NATRE region ($0.6 < \gamma < 0.7$; St. Laurent and Schmitt, 1999). Finally, our study area is characterized by a salt finger favorable regime below the mixed layer ($Ri > 1$, $R_p < 2$, $\Gamma_{\text{mix}}$).

**Fig. 2.** Average depth profiles of dissipation rates ($\varepsilon$, m$^2$ s$^{-1}$), thermal variance ($\chi$, °C s$^{-1}$), density ratio ($R_p$) and Richardson’s number log$_{10}(Ri)$.**

**Fig. 3.** Observed mixing efficiency ($\Gamma_{\text{mix}}$) and buoyancy-flux ratios ($\gamma$) dispersion plot including all the measurements obtained at the reference layer to 600 m depth. Area plot differed the mixing process involved in terms of $\Gamma_{\text{mix}}$ (turbulence: gray; salt fingers: unshaded).
layer (~ 80 m) down to 600 m is shown in Fig. 5. Also we observe that the salt finger favorable regime dominates between ~ 170 and ~ 470 m (Fig. 5). The turbulence instead acted more intensely close to the base of the mixed layer and at the boundaries of the NACW. The low surface Eddy Kinetic Energy (EKE) derived from the Sea Level Anomaly (SLA) during October 2010 for the section under study (< 20 cm² s⁻², http://www.aviso.oceanoobs.com/) corroborates the prevalence of a stratified environment in agreement to the weak vertical shear found (Ri < 1) (Le Traon and Morrow, 1999). Moreover, the contribution of the mixing processes to each layer in the water column allowed us to examine the variability between stations at the spatial scale (Fig. 5). The greatest deviation (contribution of ± 0.45) was observed at some layers (e.g. 390 m, Fig. 5), where turbulence was the main mixing process. In such cases, turbulence acts as the physical forcing factor causing system fluctuation. Similarly, although with an apparent spatial variability, the salt finger regime is the dominant mixing process. Salt vertical eddy diffusivity maintained the pattern expected according with the contribution of each mixing mechanism (Fig. 6).

Overall, vertical eddy diffusivity showed a high intermittence that is partially caused by the combination of low frequency shear and internal waves (Ruddick et al., 1997). The highest values were found at 150 m of depth, coinciding with the approximate depth where salt fingers started dominating in the water column (Fig. 6). Different studies reported that nutrient vertical diffusive transport associated with density gradients (upward) is higher in salt finger favorable systems than in those of turbulence (Hamilton et al., 1989, 1993; St. Laurent and Schmitt, 1999; Oschlies, 2002; Dietze et al., 2004). At the reference layer (30–80 m), where turbulence started dominating, the salt eddy diffusivity averaged 3.0 × 10⁻⁵ ± 3.33 × 10⁻⁹ (± SD) m² s⁻¹.

Particularly, the diffusivity values observed at station 50 were lower than those measured at all other stations. This is probably caused by the less stratified environment, which could disrupt salt fingers. The average diffusivity value obtained was in the range of those obtained in the Canary basin by other authors (1–7 × 10⁻⁵ m² s⁻¹; Hamilton et al., 1993; Ruddick et al., 1997; St. Laurent and Schmitt, 1999; Dietze et al., 2004). The diffusivity observed at the reference layer is the
effective transport of nutrients into surface waters according to the mixed layer calculated in this study.

Nonetheless, the most efficient layer for nutrient transport was located between 150 and 500 m, where a maximum of $7.94 \times 10^{-5} \pm 8.86 \times 10^{-6}$ (95% CI) m$^2$ s$^{-1}$ was observed at 300 m of depth. It seems clear that both salt fingers and turbulence coexist in our region of study and therefore need to be considered in mixing processes studies and local flux calculations.

3.2.2. Gradients and fluxes

A significant fluctuation of the vertical distribution of nutrients was observed at all stations. This is probably related to the dynamics of the Cape Ghir filament and the Canary Current (Pelegrí et al., 2005a,b). From the Sea Surface Temperature (SST) and chlorophyll satellite images (Fig. 7) the coastal upwelling affected area is clearly identified. We can observe that our hydrographic stations were close to the zone influenced by the

![Satellite images of the Cape Ghir area](image)

**Fig. 7.** Satellite images of the Cape Ghir area during which the observations were made. Left: chlorophyll in 28 October. Right: Sea Surface Temperature (SST) in 15 October. The location of the stations sampled is superimposed on the satellite images.

![Nitrate concentration isolines map](image)

**Fig. 8.** Nitrate (Nitrate plus Nitrite, N+N) concentration isolines map (mmol m$^{-3}$) at the different depths sampled. The limit between open ocean (offshore) and upwelling region (onshore) waters is shown at (a) 80 m, (b) 100 m, (c) 200 m and (d) 300 m. In (a) some of the hydrographic stations are depicted as a reference. Black arrows indicate the approximate locations of the different type of water and their origin.
Cape Ghir filament. Previous studies have located the northern boundary of the filament at ~31°N, being the latitudinal range between 31 and 34°N an area of high cross-shore interchange with the open ocean (Pelegrí et al., 2005a; Machín et al., 2006a,b; Mason et al., 2012). Using nitrate as a tracer, the boundary between coastal upwelling waters (onshore) and open ocean waters (offshore) can be clearly observed in Fig. 8.

Hydrographic stations with the highest nitrate concentrations at the reference layer (stations 26–32 and 40–44, onshore) are expected to be the densest and more nutrient-rich waters from the coastal upwelling (Jacox and Edwards, 2012; Lachkar and Gruber, 2011), which in this case is represented by the upwelling filament between Cape Ghir and Cape Sim (Fig. 8a, García-Muñoz et al., in this issue; Pelegrí et al., 2005b). The limit between both types of water was detectable from the maximum reference layer (80 m) to ~300 m (Fig. 8a–d). Indeed, nutrient vertical sections (particularly those of nitrate) confirmed and evidenced inflection points between stations where both types of waters can be observed (Fig. 9). Nitrate distributions showed shallow peaks of >2 mmol m⁻³ centered at stations 30 and 44, confirming the offshore transport of coastal upwelling waters (onshore, Fig. 9).

The distribution of nitrate and silicate observed in this study are characteristic of subtropical gyres (Sarmiento and Gruber, 2006). However phosphate showed areas where concentration gradients are not favorable for the upward flux, which is probably caused by the sinking of this nutrient or its rapid utilization in surface layer (Fig. 9) (Froelich et al., 1982; Wu et al., 2000; Mather et al., 2008; Palter et al., 2011). The nutricline was shallower at
Table 1. Average of vertical eddy diffusivity of nutrients ($K_s$), nutrient gradients ($\Delta C$), and diapycnal fluxes ($\Phi$) for nitrate, phosphate, and silicate, respectively. The numbers in parenthesis represent the Confidence Interval (CI 95%).

<table>
<thead>
<tr>
<th>Nutrient</th>
<th>Depth (m)</th>
<th>$K_s$ (mmol m$^{-2}$ d$^{-1}$)</th>
<th>Flux (mmol m$^{-2}$ d$^{-1}$)</th>
<th>$\Delta C$ (mmol m$^{-2}$ d$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate</td>
<td>528.6 (6.81)</td>
<td>3.10 $\pm$ 10$^{-1}$ (1.59 $\pm$ 10$^{-1}$)</td>
<td>4.55 $\pm$ 10$^{-2}$ (2.45 $\pm$ 10$^{-2}$)</td>
<td>6.61 $\pm$ 10$^{-2}$ (2.45 $\pm$ 10$^{-2}$)</td>
</tr>
<tr>
<td>Phosphate</td>
<td>547 $\pm$ 5</td>
<td>7.98 $\pm$ 10$^{-2}$ (8.87 $\pm$ 10$^{-2}$)</td>
<td>2.45 $\pm$ 10$^{-2}$ (2.45 $\pm$ 10$^{-2}$)</td>
<td>2.45 $\pm$ 10$^{-2}$ (2.45 $\pm$ 10$^{-2}$)</td>
</tr>
<tr>
<td>Silicate</td>
<td>678 $\pm$ 10</td>
<td>1.28 $\pm$ 10$^{-2}$ (1.54 $\pm$ 10$^{-2}$)</td>
<td>2.45 $\pm$ 10$^{-2}$ (2.45 $\pm$ 10$^{-2}$)</td>
<td>2.45 $\pm$ 10$^{-2}$ (2.45 $\pm$ 10$^{-2}$)</td>
</tr>
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4. Conclusions

Our study shows that turbulence and salt fingers coexist, and are both relevant as mixing processes, in the offshore waters of the

those stations influenced by upwelling waters. Overall the nutrient was located at 92.14 $\pm$ 28.05 m, 100 $\pm$ 25.72 m and 86.42 $\pm$ 27.62 (± SD) for nitrate, phosphate and silicate, respectively. The average vertical gradients for all stations at the reference layer (57.86 $\pm$ 8.51 m) were 0.36, $-2.55 \times 10^{-3}$ and 0.12 mmol m$^{-2}$ d$^{-1}$ for nitrate, phosphate and silicate, respectively (Table 1). The nitrate vertical gradient obtained here is significantly higher than that reported for other areas far off the coastal upwelling system towards the interior of the Canary basin (Lewis et al., 1986; Mouriño-Carballedo et al., 2011). This vertical gradient is, however, considerably lower than observed in regions of intense upwelling activity, such as the coast off Mauritania (Schaftall et al., 2010). The nutrient vertical gradients observed in our study confirm this region as a transition zone between the Northwest African coastal upwelling and the open ocean waters.

When nitrate and silicate vertical gradients are examined at the same reference level, but driving them according to their origin (offshore/onshore, Table 1), we observe that the highest gradient was related to the onshore waters (0.45 and 0.12 mmol m$^{-2}$ d$^{-1}$, respectively). Average nitrate and silicate vertical gradients for the whole water column (up to 600 m) for all the stations sampled showed favorable concentrations to the flux (upward) of nitrate and silicate towards surface waters (Table 1). In contrast, phosphate concentrations behave differently. The vertical gradient of phosphate at the reference layers indicated a deficit of this nutrient of $2.55 \times 10^{-3}$ mmol m$^{-2}$ d$^{-1}$, mostly associated with offshore waters (Table 1). Phosphate has been reported to be strongly depleted below the euphotic zone in the subtropical North Atlantic (Wu et al., 2000; Mather et al., 2008; Palter et al., 2011). However, the input of this nutrient was positive and continuous between 100 and 600 m of depth, analogous to nitrate and silicate (Table 1).

Diapycnal fluxes at the reference layer were 0.09, $-6.61 \times 10^{-4}$ and 0.03 mmol m$^{-2}$ d$^{-1}$ for nitrate, phosphate and silicate, respectively (Table 1). Despite the additional input of nutrients from the coastal upwelling, flux values at the reference layer were closer to the lowest values reported for the Canary Basin. These lower values are characteristic of stratified waters in the open ocean (e.g. Lewis et al., 1986; Planas et al., 1999; Gruber and Sarmiento, 1997; Dietze et al., 2004; Bahamón et al., 2003; Mouriño-Carballedo et al., 2011, 2004; González-Dávila et al., 2006). Notwithstanding, N$_2$ fixation rates in the subtropical Northeast Atlantic are $\sim 2-3$ orders of magnitude lower than the average rates reported for this study (Mouriño-Carballedo et al., 2011; Benavides et al., 2011; Fernández et al., 2013). This suggests that vertical turbulent diffusivity may be contributing more substantially to new production than N$_2$ fixation in this area, as supported by previous $^{15}$N-labeled nitrate and N$_2$ uptake experiments (Benavides et al., 2013).

It should be also pointed out that the low eddy diffusivity associated with the reference layer in this study and the weak influence of the upwelling during autumn might have affected the magnitude of the diapycnal fluxes measured in this time of the year (Barton et al., 1998; Pelegri et al., 2005a,b). However, in deeper layers (100–300 m) the magnitude of the fluxes is higher coinciding with a greater diffusivity related with salt fingers and favorable vertical gradients in the same direction.

In addition to the high spatial-temporal variability of the coastal transition zone of the Canary basin (Barton et al., 1998; Pelegri et al., 2005a,b; Machín et al., 2006a,b; Mason et al., 2012), there is a high uncertainty between nutrient diapycnal fluxes estimated using different methods and reference layers in the North Atlantic.
Cape Guir upwelling region (NW Africa). Therefore, micro- and fine-structure processes need to be addressed when assessing mixing processes and associated fluxes at local and regional scales. In our study, the transition zone to the northern boundary of the Cape Ghir region was particularly characterized by a salt finger favorable regime below the mixed layer (56.15 ± 15.56 m).

The greatest spatial fluctuation observed in our study was due to nutrient vertical gradients and were in close relationship with the magnitude and direction of the diapycnal flux measured. The average nutrient vertical gradients were in general high, although the effective diapycnal flux under the mixed layer (where turbulence dominates) was lower than other estimates obtained for the North Atlantic (Lewis et al., 1986; Planas et al., 1999; Gruber, 2002; Mouriño-Carballido et al., 2011). Similarly, nitrate vertical turbulent diffusion seems to play a more important contribution to new production than N\textsubscript{2} fixation in the eastern margin of the Canary basin. We also found a deficit of phosphate supply to the surface waters, which may in turn inhibit N\textsubscript{2} fixation in the northern boundary of the Northwest African Atlantic (van den Meersch et al., 2013; Yanes et al., 2013).

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References


Benavides, M., Agawa, N.S.R., Arístegui, J., Ferriol, P., Stal, L.J., 1997. Nitrogen fixation rates (Fernández et al., 2013). However at deeper layers at 300 m, where salt fingers drive mixing, the diapycnal flux increased favoring the vertical diffusive transport of nutrients. The limit between offshore and onshore waters was detected at ~300 m depth.

Finally, the known temporal variability of Canary Basin may modify the conditions that drive the magnitude and direction of nutrient eddy fluxes into surface waters. Therefore, more detailed regional studies of nutrient supply from deep to surface waters at micro- and fine-structures scale are needed.


