

## Atlantic forcing of the Mediterranean oligotrophy

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[1] The Mediterranean Sea shows a peculiar anomaly in its nutrient pattern compared to the global ocean, as there is decrease in nutrient concentration from west to east. This feature has been attributed to the antiestuarine circulation at the Strait of Gibraltar, where an eastward flow of Atlantic nutrient-poor surface waters is compensated by a westward countercurrent of Mediterranean nutrient-rich deep waters. This water exchange has been suggested as the ultimate cause for the oligotrophy of the Mediterranean basin, even though only a few studies have accurately examined the magnitude of the nutrient flux through the Strait of Gibraltar. In this work, data from the Gibraltar Fixed Time series (GIFT) between 2005 and 2008 were used to assess nutrient distributions. Applying a two-layer model of water mass exchange and using the Mediterranean outflow recorded in situ, the net export of nutrients from the Mediterranean to the Atlantic was calculated as 139 and 4.8 Gmol yr<sup>-1</sup> of nitrate and phosphate, respectively. The results also demonstrated that the Atlantic inflow is not nutrient depleted and in particular contains significant levels of phosphate, which is the limiting factor for biological productivity in the eastern Mediterranean. The distribution of the quasi-conservative parameter N\* in the western and eastern basins indicated that nitrate-deficient surface waters are transformed into phosphate-deficient bottom waters by internal cycling processes. Therefore, phosphate depletion in the Mediterranean does not have its origin in the entry of a phosphorus-impooverished Atlantic inflow through the Strait of Gibraltar.

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### 1. Introduction

[2] The Mediterranean Sea is the largest semienclosed water body on Earth. Its only connection with the rest of the world's oceans is the Strait of Gibraltar (SG) (Figure 1), which is a shallow and narrow channel with a minimum width of 14 km and an average depth of 600 m, although the shallowest point, the Camarinal Sill (CS in Figure 1) has a depth of 300 m. Water exchange within SG strongly influences the general circulation of the Mediterranean and North Atlantic [Peliz *et al.*, 2009; Béranger *et al.*, 2005] and controls the budget of elements in both basins [Ríos *et al.*, 2001; Béthoux *et al.*, 2002; Elbaz-Poulichet *et al.*, 2001; Crispì and Pacciaroni, 2009; Huertas *et al.*, 2009].

[3] The import of different compounds from the Atlantic to the Mediterranean, such as hydrocarbons, organic matter and anthropogenic CO<sub>2</sub>, has been well documented [Dachs *et al.*, 1997; Dafner *et al.*, 2001; Huertas *et al.*, 2009]. In the opposite direction, the export of substances including alkalinity [Huertas *et al.*, 2009], inorganic carbon [de la Paz *et al.*, 2008] and nutrients [Dafner *et al.*, 2003] has also been reported.

[4] The exchange of waters carrying different concentrations of substances through the SG has been regarded as the ultimate cause of the oligotrophy in the Mediterranean. It is traditionally assumed that an eastward flow of Atlantic nutrient-poor surface waters is compensated by a deep countercurrent of Mediterranean nutrient-rich waters [Coste *et al.*, 1988; Ribera d'Alcalà *et al.*, 2003]. Particularly, the ultra-oligotrophic conditions of the eastern Mediterranean (EM) caused by the scarcity of phosphate have been linked to the circulation patterns present in the straits of Sicily and Gibraltar [Krom *et al.*, 2010; Ibello *et al.*, 2010]. The case for phosphorus limitation in EM is supported by the high N:P molar ratio (~28:1) measured in deep waters, well above the oceanic Redfield ratio of 16 [Krom *et al.*, 1991]. The increasing N:P ratio in the bottom layer from west to east [Béthoux *et al.*, 1992] is considered another indication of the deficit in phosphate supply from the Atlantic.

[5] Despite the fundamental role that the nutrient exchange at the SG plays in the biogeochemistry of the Mediterranean,

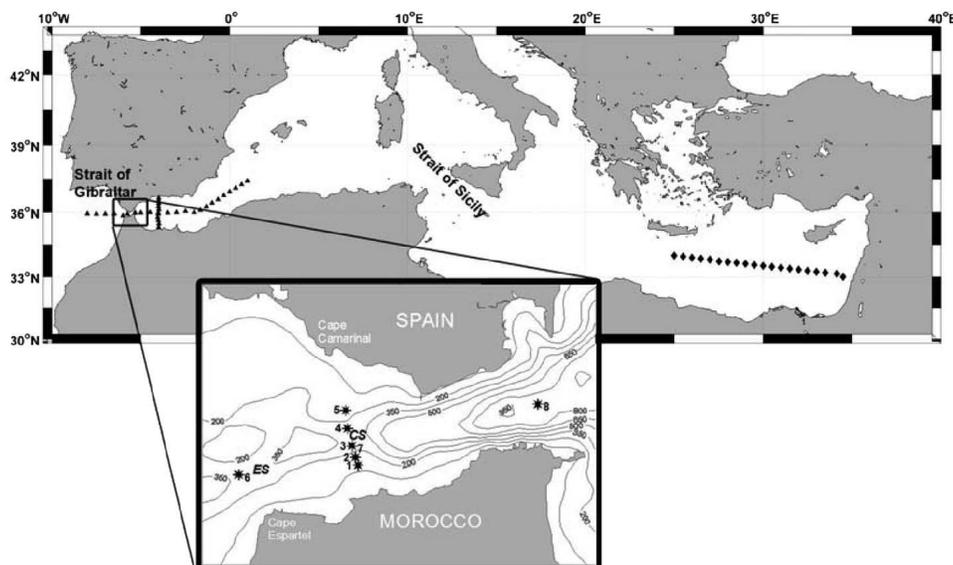
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**Figure 1.** Locations of the Strait of Gibraltar and (inset) bathymetry and sampling stations. CS and ES stand for the sills of Camarinal and Espartel, respectively. Transects sampled during the cruises SESAMEII (triangles) and SESIL02 (diamonds) in the western and eastern Mediterranean whose data were used in this study are also shown.

only a few studies have estimated the volumetric nutrient flux through the strait. Specifically, assessments of phosphate transport are few and the latest estimates yield exports that vary from  $1.6 \text{ Gmol PO}_4^{3-} \text{ yr}^{-1}$  [Dafner *et al.*, 2003] to  $16.2 \text{ Gmol PO}_4^{3-} \text{ yr}^{-1}$  [Béthoux *et al.*, 2002]. Similarly, for nitrate transport, estimates range from  $32 \text{ Gmol yr}^{-1}$  [Béthoux *et al.*, 2002] to  $350 \text{ Gmol yr}^{-1}$  [Dafner *et al.*, 2003], with intermediate values of  $71 \text{ Gmol NO}_3^-$  and  $268 \text{ Gmol NO}_3^- \text{ yr}^{-1}$  [Macias *et al.*, 2007; Ribera d'Alcalà *et al.*, 2003].

[6] Therefore, this work aims to accurately quantify the transport of nutrients between the Mediterranean Sea and the Atlantic Ocean. Extensive measurements of nutrient concentrations performed at the time series GIFT (Gibraltar Fixed Time Series) were used in combination with the in situ monitoring of Mediterranean water transport in the area. The results were used to build a nutrient balance box model for the Mediterranean Sea and elucidate the contribution of the water exchange at the SG to the nutrient status of the basin.

## 2. Material and Methods

### 2.1. Sampling

[7] Data were collected at 8 stations distributed in two perpendicular sections (Figure 1): one that goes along the longitudinal axis of the Strait and constitute the GIFT (formed by stations 6, 7 and 8) and a perpendicular section that was also sampled for intercalibration purposes. Sampling was conducted during 15 campaigns that were carried out between May 2005 and October 2008 (Table 1). At each station, a temperature and salinity profile was obtained with a Seabird 911Plus CTD probe, followed by water sampling with Niskin bottles at a minimum of five different depths that were selected on board according to the information given by the CTD cast on the position of the interface between Atlantic and Mediterranean waters (the so-called AMI).

### 2.2. Nutrient Measurements

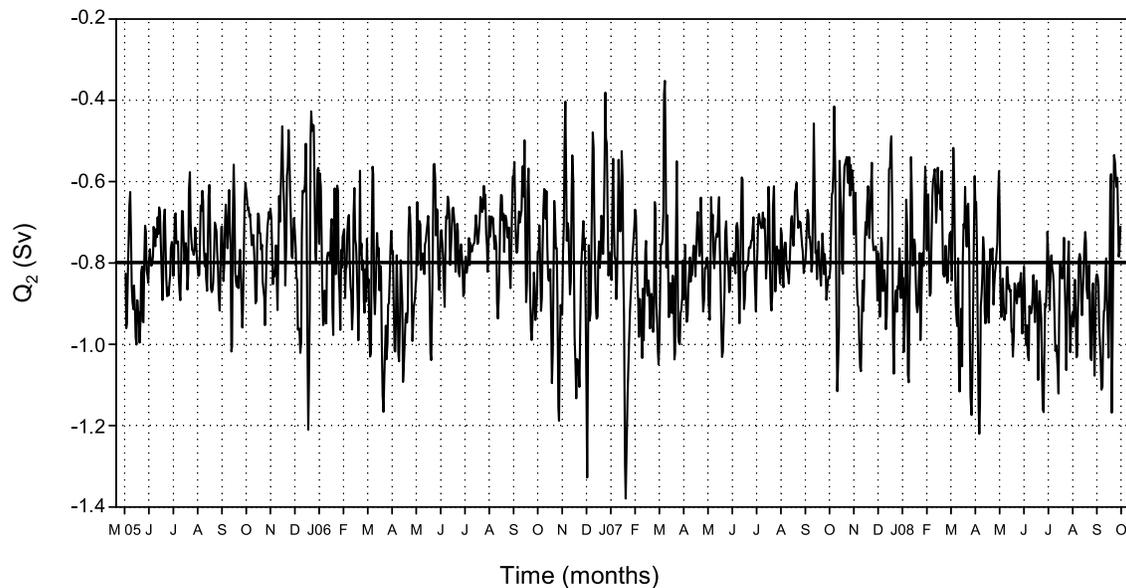
[8] Three replicates of filtered seawater (12 mL, Whatman GF/F filters) were taken at each station and stored at  $-20^\circ\text{C}$  for inorganic nutrient analysis. Concentrations of nitrate plus nitrite (hereafter referred as nitrate) and phosphate were measured in the laboratory using a Skalar San++ System auto-analyser and the techniques of Grasshoff *et al.* [1983]. The standard deviation for the mean of all the replicates was under  $0.06$  and  $0.01 \mu\text{mol kg}^{-1}$  for nitrate and phosphate, respectively.

### 2.3. Water Transport Estimations

[9] Water circulation in the SG can be approximated as a two-layer system formed by a surface eastward Atlantic Inflow (AI) and a deep westward Mediterranean Outflow (MOW). The transition from one layer to the other takes place gradually through the AMI, which appears as a strong

**Table 1.** Acronyms, Dates, and Ships Used for the Campaigns Considered in This Study

Campaign ID	Date	Ship
CARBOGIB1	02–05 May 2005	RV <i>Al Amir Moulay Abdellah</i>
CARBOGIB2	07–09 Sep 2005	RV <i>Al Amir Moulay Abdellah</i>
CARBOGIB3	12–14 Dec 2005	RV <i>Al Amir Moulay Abdellah</i>
CARBOGIB4	20–22 Mar 2006	RV <i>Al Amir Moulay Abdellah</i>
CARBOGIB5	21–23 May 2006	RV <i>Al Amir Moulay Abdellah</i>
GIFT3	23–24 Nov 2006	BO <i>García del Cid</i>
CARBOGIB6	13–15 Dec 2006	RV <i>Al Amir Moulay Abdellah</i>
CARBOGIB7	07–08 May 2007	RV <i>Al Amir Moulay Abdellah</i>
CARBOGIB8	04–05 Jul 2007	RV <i>Al Amir Moulay Abdellah</i>
CARBOGIB9	06–07 Nov 2007	RV <i>Al Amir Moulay Abdellah</i>
SESAME1	13–14 Apr 2008	BO <i>Regina Maris</i>
SESAME2	27–28 Jul 2008	BO <i>Regina Maris</i>
SESAME3	25–26 Sep 2008	BO <i>García del Cid</i>
P3A2_1 <sup>ST</sup> _LEG	12–13 Oct 2008	RV <i>Hesperides</i>
P3A2_2 <sup>ND</sup> _LEG	20–21 Oct 2008	RV <i>Hesperides</i>



**Figure 2.** Time series of the Mediterranean water transport ( $Q_2$ ) measured from May 2005 to September 2008. Solid horizontal line marks the average value of  $-0.80$  Sv.

pycnocline that undergoes striking vertical oscillations mainly due to tidal flow-topography interaction. The AI is mainly formed by the mixing of the North Atlantic Surface Waters (NASW, salinity  $\sim 36.46$ ) and North Atlantic Central Water (NACW, salinity  $< 36.06$ ). Similarly, the MOW is a mixture of intermediate and deep waters residing in the Mediterranean Sea, basically Levantine Intermediate Water (LIW) formed in the EM, which flows across the Strait of Sicily into the western basin, and the Western Mediterranean Deep Water (WMDW) formed in the Gulf of Lions. Due to the complexity of the hydrodynamic processes within the SG, water masses contributing to the AI or to the MOW appear either intermittently, as in the case of the less abundant NACW in the AI [Gascard and Richez, 1985; Macías *et al.*, 2007], or mixed in changing proportions throughout the year, as in the WMDW to the MOW [García-Lafuente *et al.*, 2007].

[10] The negative freshwater and buoyancy fluxes in the Mediterranean basin drive the baroclinic exchange in SG necessary to preserve the volume and salt content of the sea. This exchange is inverse estuarine with an upper AI ( $Q_1$ ) and an underflow  $Q_2$  of colder and saltier Mediterranean water, both on the order of  $0.8$  Sv ( $1 \text{ Sv} = 10^6 \text{ m}^3 \text{ s}^{-1}$ ) (Figure 2), the later plunging down in the Gulf of Cadiz (GoC) to become neutrally buoyant before spreading into the North Atlantic [Baringer and Price, 1997; Ambar *et al.*, 2002]. A long-term barotropic flow  $Q_0 = Q_1 + Q_2$  of  $0.038 \pm 0.007$  Sv is needed to balance the water deficit of the Mediterranean [Soto-Navarro *et al.*, 2010].

[11] In this work,  $Q_2$  was continuously measured at station 6 (Figure 1) since hydraulic control is nearly permanent in this site [Sánchez-Román *et al.*, 2009; Sannino *et al.*, 2009], a fact that facilitates MOW computations [García-Lafuente *et al.*, 2007].  $Q_2$  was estimated from data recorded with a mooring line equipped with an uplooking ADCP, a pointwise currentmeter and an autonomous CTD probe located at 20 m, 15 m and 10 m above seafloor, respectively. The ADCP resolves 40 bins, each 8 m thick, at a sampling rate of 30 min [Sánchez-Román *et al.*, 2009].

## 2.4. Exchange of Nutrients Through the Strait of Gibraltar

[12] In order to assess nutrient transport through the SG, the two water masses that are exchanged in the area must be properly identified. Salinity is considered the most suitable parameter for defining water masses in the region [Dafner *et al.*, 2003; Huertas *et al.*, 2009; García-Lafuente *et al.*, 2009]. Accordingly, the interface was identified here by fixed salinity values: 37.0 and 37.8 on the western and eastern sides of the Strait, respectively. These reference values are based on the entrainment that the fast-flowing layer exerts on the slow-flowing one. West of CS the Mediterranean layer is faster and entrains Atlantic water, which diminishes the salinity of the outflow ( $S = 37.0$ ). East of the CS the fast flowing Atlantic layer entrains Mediterranean water, making the AI saltier ( $S = 37.8$ ). At either side of the SG, water characterized by a lower salinity than the selected limit was integrated into the AI whereas the remaining water column with higher salinity values was incorporated into the MOW.

[13] The net flux of nutrients ( $F_N$ ) through the SG was obtained using the equation:

$$F_N = F_2 - F_1 = (\rho_2 \times Q_2 \times N_{T2}) - (\rho_1 \times Q_1 \times N_{T1}) \quad (1)$$

where  $F_2$  and  $F_1$  represent the nutrient flux into the Mediterranean and the Atlantic respectively and  $\rho$ ,  $Q$  and  $N$  stand for water density, volume transport and nutrient concentration. Average densities of 1029 and 1027  $\text{kg m}^{-3}$  were taken for the MOW and AI, respectively. Likewise, as nutrient concentration and current velocity were acquired at different rates, average values of both variables were introduced in equation (1). Mean concentrations of nutrients were calculated for each layer on both sides of the Strait (Table 2) and the average estimate of  $Q_2$  was obtained from the time series of the transport of MOW.  $Q_1$  was subsequently calculated from  $Q_2$  (Table 2) considering the fresh water balance in the Mediterranean basin. Uncertainties were determined using the variability of the measured fluxes that was coupled to the

**Table 2.** Average Concentrations and Standard Deviation of Nitrate and Phosphate in the Atlantic and Mediterranean Layers at the Western and Eastern Sides of the Strait of Gibraltar, Represented by Stations 6 and 8, Respectively<sup>a</sup>

	Water Mass	Q (Sv)	Nitrate ( $\mu\text{mol kg}^{-1}$ )	Phosphate ( $\mu\text{mol kg}^{-1}$ )	N* ( $\mu\text{mol kg}^{-1}$ )
Station ID					
6	AI	$0.84 \pm 0.02$	$3.1 \pm 0.3$	$0.29 \pm 0.03$	$-1.5 \pm 0.1$
6	MOW	$-0.80 \pm 0.02$	$8.6 \pm 0.5$	$0.49 \pm 0.04$	$0.8 \pm 0.2$
8	AI	$0.80 \pm 0.02$	$3.0 \pm 0.5$	$0.25 \pm 0.04$	$-1 \pm 0.1$
8	MOW	$-0.76 \pm 0.02$	$8.8 \pm 0.6$	$0.48 \pm 0.05$	$1.1 \pm 0.1$
$F_N$ ( $\text{kmol s}^{-1}$ )			-4.4	-0.15	-1.9
Uncertainty ( $\text{kmol s}^{-1}$ )			0.1	0.01	0.04

<sup>a</sup>Both stations were sampled 15 times. Water transport variability is expressed as the confidence interval of the average value of the series. Net fluxes ( $F_N$ ) of nutrients and N\* between the Atlantic and the Mediterranean are also indicated. Uncertainty estimated by an error propagation analysis and associated to the flux calculation is given.

propagated uncertainties due to nutrient concentrations through perturbations ( $n = 100$ ).

### 3. Results and Discussion

#### 3.1. Water Flows Through the Strait of Gibraltar

[14] The transport of MOW ( $Q_2$ ) during the study period, after removing the tidal contribution, is plotted in Figure 2. It is characterized by a marked subinertial variability (time scale of few days to weeks) whose origin is likely due to atmospheric pressure variations over the Mediterranean Sea and to local and remote winds to a lesser extent [García-Lafuente *et al.*, 2007; Sánchez-Román *et al.*, 2009]. From this series ( $n = 1270$ ), a mean  $Q_2$  of  $-0.80$  Sv was obtained (Figure 2), which is in good agreement with previous estimates [Huertas *et al.*, 2009]. The resulting confidence interval ( $0.02$  Sv in Table 2) was mainly due to subinertial variability.

#### 3.2. Nutrient Distribution in the Strait of Gibraltar

[15] The spatial distribution of nitrate and phosphate along with the distinctive thermohaline properties of the water masses present in the SG is displayed in Figure 3. Vertical profiles were obtained through data interpolation. At the western entrance of the Strait, the presence of MOW is evident between 260 and 358 m (Figure 3b) as seen by its salinity ( $>38$  in Figure 3a) and thermal signature ( $\sim 13^\circ\text{C}$ ). Here, the upper layer corresponds to the AI, with a characteristic salinity of about 36.46 (Figure 3a) and a temperature range between  $18^\circ\text{C}$  and  $15^\circ\text{C}$ , situated between 0 and 200 m (Figure 3b). The AMI is also distinguishable as a prominent halocline between both layers (Figure 3a) and displays a mean vertical temperature variation of  $2^\circ\text{C}$  ( $15$ – $13^\circ\text{C}$  in Figure 3b). Due to topography, its position slopes upward toward the eastern side of the Strait (Figure 3a), as the AI accelerates in, and especially east of CS as it entrains the Mediterranean water. The Mediterranean layer thus occupies a larger volume, extending to about 120 m below the surface of the water column (Figures 3a and 3b).

[16] Nitrate and phosphate distributions were characterized by an increasing vertical gradient everywhere in the channel, which reflects the confluence of water masses (Figures 3c and 3d). In particular, nitrate exhibited minimum values ( $\sim 1.2 \mu\text{mol kg}^{-1}$ ) within the upper 50 m of the water column in the westernmost part of the Strait and increased toward the east to reach concentrations of about  $3 \mu\text{mol kg}^{-1}$  (Figure 3c). Overall, the average  $\text{NO}_3^-$  concentration in the AI penetrating into the Mediterranean was  $3.1 \pm 0.3 \mu\text{mol kg}^{-1}$  ( $n = 54$  in waters with  $S < 37.8$  at station 8; see

Table 2). Much higher levels of nitrate ( $\sim 9 \mu\text{mol kg}^{-1}$ ) were detected in the MOW, with the maximum concentration being observed above the seafloor in the easternmost part of the Strait (Figure 3c). The average  $\text{NO}_3^-$  concentration in the MOW was  $8.8 \pm 0.6 \mu\text{mol kg}^{-1}$  ( $n = 38$  in waters with  $S > 37$  at station 6; see Table 2).

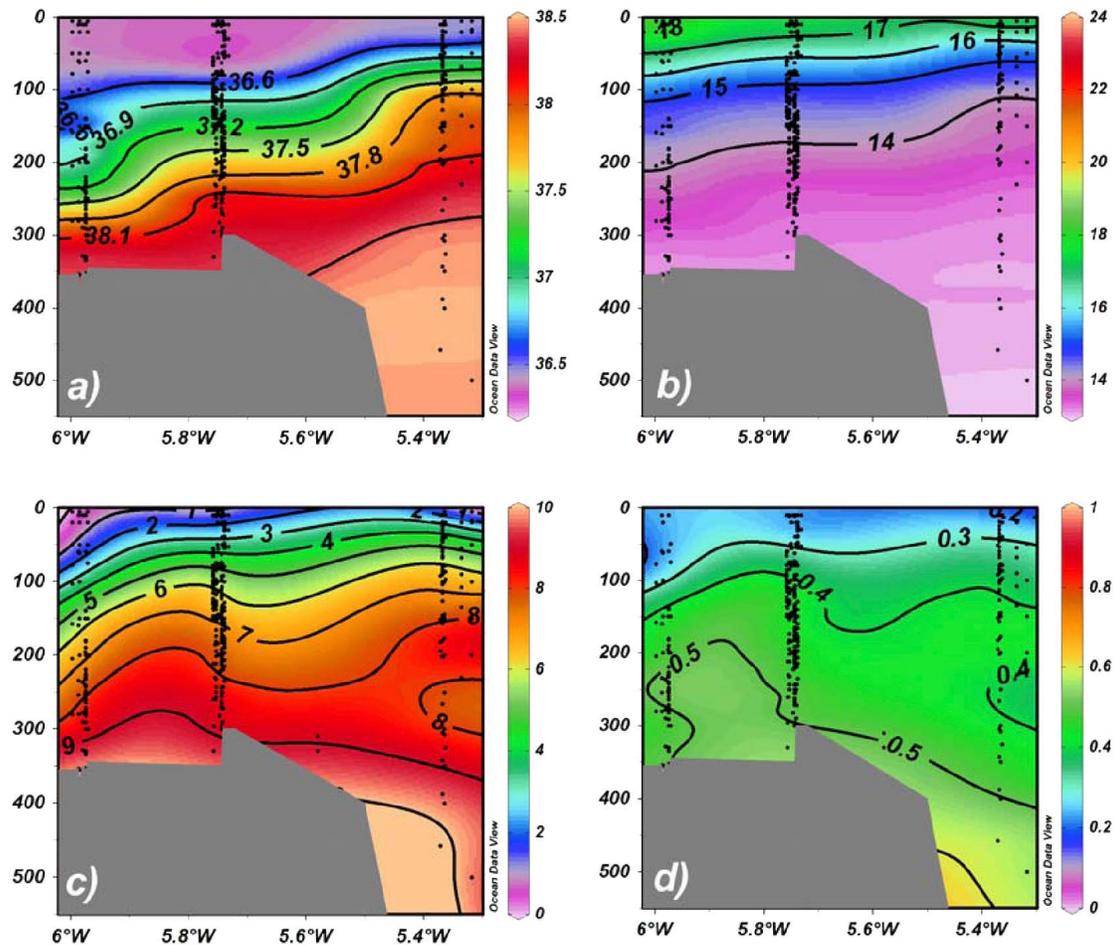
[17] In contrast, phosphate concentrations were constant in surface waters at a value of about  $0.3 \mu\text{mol kg}^{-1}$  (Figure 3d). Throughout the whole channel, the AI contained lower phosphate levels than those found in the MOW and average  $\text{PO}_4^{3-}$  concentrations of  $0.25 \pm 0.04 \mu\text{mol kg}^{-1}$  and  $0.49 \pm 0.04 \mu\text{mol kg}^{-1}$  were found within each layer, respectively (Table 2). A slight reduction in phosphate was observed toward the east in the upper 100 m of the water column (Figure 3d). This may be related to the different  $\text{PO}_4^{3-}$  concentrations found in the two basins connected by the SG; phosphate levels are much higher in surface waters of the GoC [Navarro *et al.*, 2006] than in the Alboran Sea [Karafistan *et al.*, 2002]. Conversely, nitrate is generally higher in the Alboran [Ramírez *et al.*, 2005; Prieto *et al.*, 2009], which explains the higher concentrations detected in surface waters at the eastern entrance of the Strait (Figure 3c). These observations are also supported by recent modeling results [Skiris and Beckers, 2009]. The low variability of the average nutrients concentration (Table 2) reflects the insignificance of seasonality on the nutrient pattern in the SG.

#### 3.3. Exchange of Nutrients Between the Mediterranean and the Atlantic

[18] Nutrient exchange through the SG was obtained by applying equation (1). The data summarized in Table 2 indicate that a net  $\text{NO}_3^-$  export of  $4.4 \pm 0.1 \text{ kmol s}^{-1}$  ( $139 \pm 3 \text{ Gmol yr}^{-1}$ ) occurs between the Mediterranean and the Atlantic. Transport of phosphate is considerably lower with a net export of  $0.15 \pm 0.01 \text{ kmol s}^{-1}$  ( $4.8 \pm 0.3 \text{ Gmol yr}^{-1}$ ).

#### 3.4. Nutrient Balance in the Mediterranean Sea

[19] Most nutrients budgets available for the Mediterranean Sea imply that its oligotrophy is due to the anti estuarine circulation in the SG [Béthoux *et al.*, 2002; Ibello *et al.*, 2010; Ribera d'Alcalà *et al.*, 2003]. This assumption is also applied to nutrient balances in the western Mediterranean (WM) [Schroeder *et al.*, 2010]. Similarly, the ultra-oligotrophy of the Levantine basin has been attributed to the anti estuarine regime in the Straits of Sicily [Krom *et al.*, 2004, 2010]. In contrast, numerical models suggest that the circulation pattern in the Straits is not sufficient to explain the trophic status of the EM [Crispi *et al.*, 2001].



**Figure 3.** Distribution of (a) salinity, (b) potential temperature ( $\theta$ ,  $^{\circ}\text{C}$ ), (c) nitrate ( $\mu\text{mol kg}^{-1}$ ), and (d) phosphate ( $\mu\text{mol kg}^{-1}$ ) in the Strait of Gibraltar. Contouring was done through the DIVA Gridding interpolation.

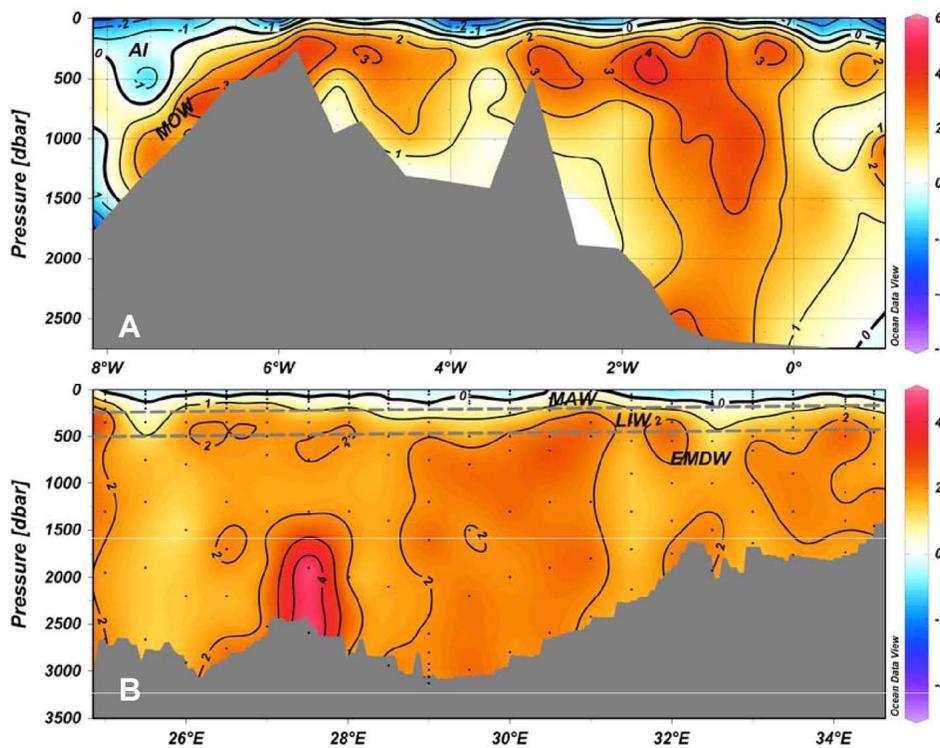
[20] Still, estimates of nutrient exchange through the SG are largely discrepant [Coste *et al.*, 1988; Béthoux *et al.*, 2002; Dafner *et al.*, 2003; Ribera d'Alcalà *et al.*, 2003; Macías *et al.*, 2007]. This is especially true for phosphate transport, which was last assessed a decade ago [Dafner *et al.*, 2003]. The analysis performed here helps put constraints on these estimates, as it is based on extensive measurements recently collected in the area, combined with the in situ monitoring of water mass transport. This approach reduced the uncertainty that arises when dispersed measurements are combined for computation of the exchange rate.

[21] The resulting transport rates of nitrate and phosphate from the Mediterranean to the Atlantic (Table 2) fall within the range of others reported in the region. Nonetheless, our results also show that Atlantic waters crossing the SG are not nutrient depleted (Figures 3c and 3d and Table 2). In fact, the AI has a nutrient content that is high enough to sustain phytoplankton growth, exceeding phytoplankton semi-saturation constants for nitrate ( $K_s = 0.5 \mu\text{M}$ ) [Eppley *et al.*, 1969] and phosphate ( $K_s = 0.05 \mu\text{M}$ ) [Davies and Sleep, 1989]. Furthermore, phosphate is in excess with respect to nitrate within this layer, as indicated by the N:P ratio found on both sides of the Strait (11:1 and 12:1 at stations 6 and 8 respectively). This molar ratio is well below the Redfield

stoichiometry, which is only surpassed inside the MOW (17.5:1 at station 6).

[22] This suggests that processes occurring within the WM impact the rate of nutrient transport from the Strait of Sicily to Gibraltar. Specifically, Karafistan *et al.* [2002] and Ribera d'Alcalà *et al.* [2009] report that surface waters passing through the Straits of Sicily (0–50 m) are depleted in nitrate and phosphate; very different from the pattern described in the SG.

[23] However, interpretation of deviations in the Redfield ratio is difficult, as this coefficient is highly nonlinear, especially at low nutrient concentrations, and therefore not conservative. The amount of available fixed nitrogen can be strongly affected by biological processes, such as denitrification and nitrogen fixation by diazotrophic organisms, whereas phosphorus concentrations are controlled by the balance between river inputs and loss to sediments. Hence, the quasi-conservative parameter  $N^*$  has been suggested as an alternative to explain nutrient relationships in certain ocean regions as it depicts the net influence of the aforementioned processes on nitrate distribution in a consistent manner [Gruber and Sarmiento, 1997].  $N^*$  is defined as the linear combination of nitrate and phosphate that eliminates most of the effect of nitrification of organic matter, with the



**Figure 4.** Spatial distribution of  $N^*$  ( $\mu\text{mol kg}^{-1}$ ) in two regions of the (a) western and (b) eastern Mediterranean in September 2008. Data were collected during the campaigns SESAMEII and SESIL02 and are available in the SESAME project database (<http://isramar.ocean.org.il/SESAMECruises/map.asp>). The different water masses present in both regions are indicated by their acronyms (AI, MOW, MAW, LIW, and EMDW). Horizontal dashed gray lines in Figure 4b also denote their position in the water column in the eastern basin.

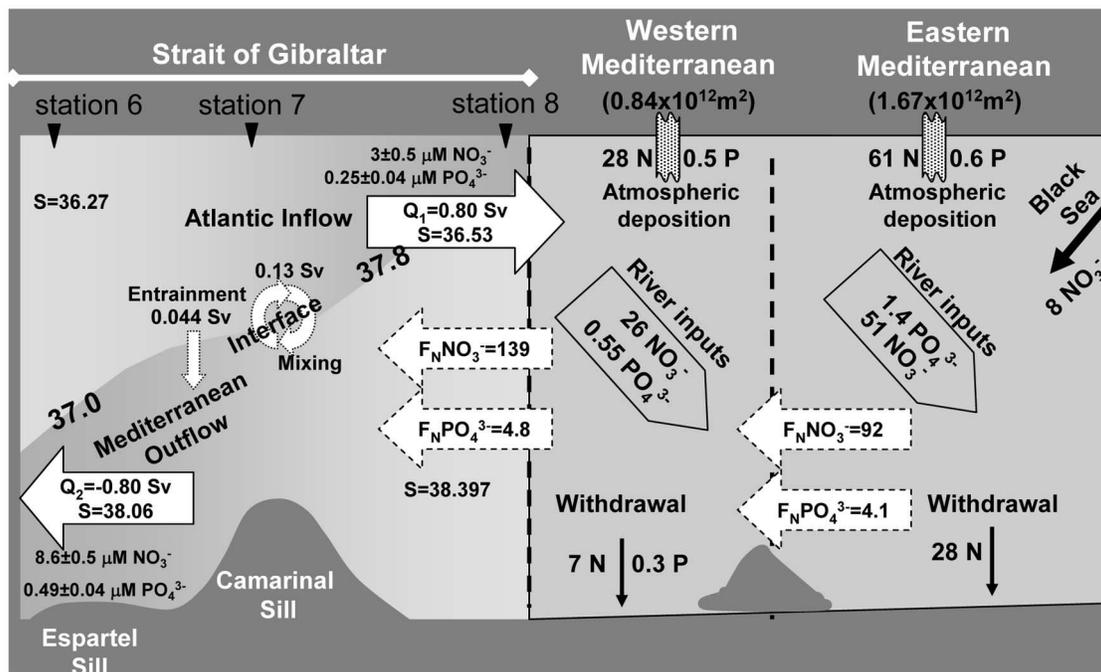
remaining variability being primarily caused by the combined effect of denitrification and nitrogen fixation plus atmospheric deposition and river inflow.

[24] The spatial pattern of  $N^*$  was analyzed in two representative regions of the WM and EM using data collected in September 2008 and gathered by the SESAME project (Figure 1).  $N^*$  distribution along a longitudinal transect connecting the GoC and the South WM and sampled during the SESAMEII cruise (Figures 1 and 4a), shows that surface waters are characterized by negative  $N^*$  values. In particular,  $N^*$  remains negative from the surface to a depth of 700 m in the GoC, which is an indication of a deficiency in nitrate relative to phosphate in a vast portion of the mesopelagic zone [Navarro *et al.*, 2006]. The zero  $N^*$  contour, which represents the Redfield stoichiometry, rises toward the surface in the SG, with a minimum ( $\sim -3 \mu\text{mol kg}^{-1}$ ) appearing in surface waters at its western entrance where the lowest nitrate concentrations are always detected (Figure 3c). A secondary  $N^*$  low is found within the upper 250 m of the Alboran Sea, where substantial rates of primary production are regularly found [Skirris and Beckers, 2009] and a lower than Redfield N:P ratio is observed [Ramírez *et al.*, 2005]. This distribution confirms that the entire photic zone of the transition area between the Atlantic and the WM is nitrate-deficient with respect to phosphate. In contrast, the MOW exhibits positive  $N^*$  values close to  $4 \mu\text{mol kg}^{-1}$ , which is in agreement with the  $N^*$  levels of the LIW that is the main component of this water layer [Minas *et al.*, 1991]. The

Mediterranean tongue carrying the high  $N^*$  signal spreads into the GoC (Figure 4a) and, near  $8^\circ\text{W}$ , it appears in two well-reported veins of MOW flowing at depths of around 700 m and 1100 m [Ambar and Howe, 1979]. The near zero  $N^*$  values observed in deeper waters of the Alboran Sea (Figure 4a) can be attributed to the influence of mesoscale processes, such as the intense cyclonic vorticity generated by the entry of the AI that causes the upwelling of nutrient enriched deep waters [Skirris and Beckers, 2009]. As a result, the vertical flux of organic matter produced by the enhanced productivity triggers bacterial growth below the photic zone, which generates nutrients with a Redfield stoichiometry [Minas *et al.*, 1991]. It should be noted that denitrification in subsurface waters in upwelling regions cannot be ignored [Deutsch *et al.*, 2001], which would also contribute to the decrease in  $N^*$  (Figure 4a). Using all of the measurements collected in the SG during more than 3 years, the net export of  $N^*$  from the Mediterranean to the Atlantic is  $61.2 \text{ Gmol yr}^{-1} (\pm 0.8)$  (Table 2).

[25] Altogether, these results indicate that nitrogen-impooverished surface waters are transformed into phosphate-deficient bottom waters in the Mediterranean, but the deficit of phosphate is not caused by the entry of a phosphorus-depleted AI through the SG.

[26] This conclusion is further supported by the  $N^*$  distribution in the EM (Figure 4b). In this case, data were acquired during the SESIL02 cruise carried out in the Levantine Basin (Figure 1). The upper 200 m of the water



**Figure 5.** A box model of the Mediterranean Sea nutrient balance. Average concentrations of nitrate and phosphate (in  $\mu\text{M} \pm \text{SD}$ ) in the Atlantic inflow and the Mediterranean outflow in the Strait of Gibraltar are indicated. Both layers are separated by an interface (AMI), which is identified by salinity values of 37.0 and 37.8 on the western and eastern sides of the strait, respectively. Entrainment and mixing in the AMI is given in Sv. Transports of MOW ( $Q_2$ ) and AI ( $Q_1$ ) through the strait (in Sv) along with the average salinity in each layer are provided within solid arrows that mark direction of flows. Dashed arrows denote next fluxes of nitrate ( $F_N \text{NO}_3^-$ ) and phosphate ( $F_N \text{PO}_4^{3-}$ ) across the Straits of Sicily (data from *Schroeder et al.* [2010]) and Gibraltar (this work). Fluxes and nutrient inputs and outputs are expressed in  $\text{Gmol yr}^{-1}$  (references given in the text).

column in the region has negative  $N^*$  values, confirming nitrate deficiency relative to phosphate in surface waters. This layer corresponds to the Modified Atlantic Water (MAW) that flows at the surface through the Straits of Sicily [*Ribera d'Alcalà et al.*, 2003] and still conserves its original nitrogen deprivation. In contrast, the water column below 250 m formed by the LIW (200–500 m) and the Eastern Mediterranean Deep Water (EMDW  $\sim 800$  m), exhibits positive  $N^*$  values (Figure 4b).

[27] Because the Mediterranean basin is a region of deep water mass formation, nutrient inputs from the bottom are unlikely and vertical modifications in the nutrient ratios must be related to external sources. Figure 5 presents a nutrient balance box model for the Mediterranean in which the quantitative contribution of sources and sinks of nutrients has been indicated. It is clear that the net nitrate export through SG (Table 2) is substantially higher than that recently measured through the Straits of Sicily, equivalent to  $92 \text{ Gmol yr}^{-1}$  [*Schroeder et al.*, 2010]. Therefore, an enrichment of  $47 \text{ Gmol yr}^{-1}$  of  $\text{NO}_3^-$  must occur within the WM. A recent basin-wide study on  $\text{N}_2$  fixation has demonstrated that diazotrophy is an insignificant nitrate source in the Mediterranean [*Ibello et al.*, 2010]. In contrast, recent studies suggest that river inputs and atmospheric deposition supply  $26$  and  $28 \text{ Gmol yr}^{-1}$  of  $\text{NO}_3^-$ , respectively [*Ludwig et al.*, 2009; *Markaki et al.*, 2010]. This implies that in the WM,  $7 \text{ Gmol yr}^{-1}$  of nitrate must be sequestered by

sediment burial and/or denitrification. Both mechanisms are likely to occur, particularly in poorly ventilated regions of the water column (sapropel layers [*Filippelli et al.*, 2003]) or in seafloor sediments adjacent to major rivers that allow for oxygen consumption and heterotrophic denitrification, as it has been found in certain areas of the EM [*Krom et al.*, 2010].

[28] Also in the EM, rivers and atmospheric inputs supply  $51$  and  $61 \text{ Gmol NO}_3^- \text{ yr}^{-1}$  [*Ludwig et al.*, 2009; *Markaki et al.*, 2010], which are accompanied by an input of  $8 \text{ Gmol NO}_3^- \text{ yr}^{-1}$  from the Black Sea [*Çolpan Polat and Tugrul*, 1995]. Therefore, assuming steady state, these additional inputs into the EM suggests that there is a further removal of  $28 \text{ Gmol yr}^{-1}$  by both sediment burial and denitrification. This sink is lower than the previous estimate reported in the literature ( $37 \text{ Gmol yr}^{-1}$  [*Krom et al.*, 2010]), which was deduced by assuming an export through the Strait of Sicily of  $142 \text{ Gmol NO}_3^- \text{ yr}^{-1}$ .

[29] On the contrary, phosphate remains quite stable in the WM (Figure 5) and the export through the Straits of Sicily ( $4.1 \text{ Gmol yr}^{-1}$  [*Schroeder et al.*, 2010]) and Gibraltar (Table 2 and Figure 5) is almost identical. Phosphate inputs by river discharges and atmospheric deposition only represent  $0.5$  [*Ludwig et al.*, 2009] and  $0.55 \text{ Gmol yr}^{-1}$  [*Markaki et al.*, 2010] respectively, which results in very low rates of removal by sediments ( $\sim 0.3 \text{ Gmol yr}^{-1}$ ). In the EM, an organic phosphorus sediment burial flux of  $1 \text{ Gmol yr}^{-1}$  has

been indirectly inferred [Krom *et al.*, 2004], which would not be compensated by the recent estimates of fluvial and atmospheric inputs of 1.4 and 0.6 Gmol PO<sub>4</sub><sup>3-</sup> yr<sup>-1</sup>, respectively [Ludwig *et al.*, 2009; Markaki *et al.*, 2010], leading to unbalanced export through the Straits of Sicily, which is not observed.

[30] This budget highlights the fact that phosphate inputs are not all accounted for in the EM. In the Levantine basin, some phosphorus chemical species may have been underestimated, as it is very difficult to separate labile P from nonlabile P [Krom *et al.*, 2010]. Moreover, the contribution of the Black Sea certainly needs to be updated.

[31] Nevertheless, the role of the Strait of Gibraltar in the nutrient cycle of the Mediterranean is now clearer. Our data show that the Atlantic fuels the Mediterranean with phosphate. External nitrogen-enriched inputs determine the non-Redfield stoichiometry of the Mediterranean, creating a nutrient imbalance, particularly in the EM. Therefore, the input of nutrient-depleted Atlantic waters does not induce the phosphate driven oligotrophy of the Mediterranean.

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