The N:Si:P molar ratio in the Strait of Gibraltar

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[1] All existing descriptions of nutrient distributions in the Strait of Gibraltar suggest that the Atlantic water brings to the Mediterranean Sea nutrients in the Redfield ratio (N:Si:P = 16:15:1). Here, the N:Si:P molar ratios ($\pm$ Standard Error), obtained in April 1998, are used to show that in the Atlantic water at the western entrance of the Strait this ratio is lower ($13.8(\pm 0.5):12.1(\pm 1.0):1$) than the classical Redfield ratio; it is close to the Redfield ratio in the middle of the Strait ($15.6(\pm 0.6):10.7(\pm 0.9):1$), and increases dramatically to $23.6(\pm 3.4):29.1(\pm 4.5):1$ at the eastern entrance of the Strait. In the Mediterranean water, the N:Si:P ratio has a quite similar trend with $31.5(\pm 6.0):26.5(\pm 3.6):1$ in the east, $20.4(\pm 0.2):31.5(\pm 11.1):1$ in the middle and $18.1(\pm 0.6):17.6(\pm 0.7):1$ in the west of the Strait. The physical and biological processes that account for the observed spatial variability of the N:Si:P ratio along the Strait are identified. We estimated that in the Atlantic water entering the Mediterranean Sea, about 84% of the variability in N:Si:P molar ratio is due to biological and 16% to physical processes. **INDEX TERMS:** 4845 Oceanography: Biological and Chemical: Nutrients and nutrient cycling; 4283 Oceanography: General: Water masses; 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); **KEYWORDS:** nutrient, Redfield molar ratio, the Strait of Gibraltar. **Citation:** Dafner, E. V., R. Boscolo, and H. L. Bryden, The N:Si:P molar ratio in the Strait of Gibraltar, *Geophys. Res. Lett.*, 30(10), 1506, doi:10.1029/2002GL016274, 2003.

1. Introduction

[2] The molar ratio between nitrate, silicate and phosphate in marine phytoplankton and in deep oceanic waters is generally constant (N:Si:P = 16:15:1) and is known as the Redfield ratio [Redfield *et al.*, 1963]. In this ratio phytoplankton consume nutrients from seawater, and bacteria mineralize organic nutrients to inorganic. One of the unresolved paradoxes of the Mediterranean Sea is the high N:Si:P ratio in deep waters: 24:32:1 in the Eastern and 22:19.5:1 in the Western Basins [Béthoux *et al.*, 2002]. Nitrate, silicate and phosphate concentrations in the Mediterranean Sea are controlled by the exchange through the Straits of Gibraltar and Bosphorus, by the atmospheric deposition and by river discharge.

[3] To explain these high ratios we need to understand the balance of nutrients in the Mediterranean Sea. The

Atlantic water is one component of this balance that is still poorly understood [Béthoux *et al.*, 1998]. Despite the fact that the Atlantic water entering the Mediterranean Sea is depleted in nutrients [e. g., Minas *et al.*, 1991; Turley, 1999], all existing descriptions of nutrients in the Strait suggest that these nutrients are related in the Redfield ratio [Béthoux *et al.*, 2002]. Most of these observations were made on the western entrance of the Strait, and they were applied to the Atlantic water in the Mediterranean Sea [Béthoux *et al.*, 2002].

[4] High Redfield ratios (30 to 50) found in the Alboran Sea - Algerian Current have been interpreted as a signature of earlier nutrient uptake that has taken place within a high N:P environment [Raimbault and Coste, 1990]. Minas and Minas [1995] have emphasized that the water circulation near Europa Point on Gibraltar and in the Alboran Sea determines recycling of nutrients in the Mediterranean Sea, which maintains the high N:P tendency over the whole basin. Here we show that N:Si:P ratio in the Atlantic water in the eastern entrance of the Strait is higher than 16:15:1, and that this ratio increases dramatically from the western to the eastern entrance of the Strait. In the Mediterranean water the N:Si:P ratio has a quite similar behavior.

2. Material and Methods

[5] Samples were collected in the Strait of Gibraltar area between 12 and 18 April 1998 on board of the *RRV Discovery*, cruise 232 (Figure 1). A CTD rosette system (Seabird) equipped with 10 L Niskin bottles was used. Stations were chosen to cover a variety of waters from western (in the Spartel sill area) and eastern (in the Western Alboran Sea) entrances of the Strait, and in the middle of the Strait (Tarifa Narrows). The bottles were fired at the depths of maximum or minimum distribution of temperature, salinity, oxygen and fluorescence, within and between different water bodies and at the interface layer between the Atlantic inflow and Mediterranean outflow. Samples were also taken at few meters from the bottom. A detailed description of the depth profiles and bottled sampling are shown in Dafner *et al.* [2001].

[6] The Winkler whole bottle titration method with amperometric endpoint detection for dissolved oxygen determination was used [Culbertson and Huang, 1987]. Water samples for nitrate plus nitrite (hereafter referred as nitrate), silicate, and phosphate analysis were collected after CFC, dissolved oxygen and total organic carbon samples. Chemical constituents were measured on board immediately after sampling. All nutrients were analyzed with a Chemlab Auto Analyser II coupled to a Digital-Analysis Microstream data capture and reduction system [Hydes, 1984]. Specification of the chemical analyses, including precision, accuracy, and detection limits are provided in Table 1. In this

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Figure 1. Location of sampling stations in the Strait of Gibraltar during cruise 232 on board of the *RRV Discovery* (12–18 April, 1998). To the east of the Strait lies the Alboran Sea, the western-most basin of the Mediterranean Sea. To the west of the Strait lies the Gulf of Cádiz, an embayment of the Northeast Atlantic Ocean.

work, data on phytoplankton composition and biomass were taken from [Gómez *et al.*, 2000].

3. Results and Discussion

[7] The study area and the hydrographic conditions found in the Strait of Gibraltar in April 1998 have been already described in greater detail [Dafner *et al.*, 2001]. The Redfield molar ratios based on individual nutrient concentrations (Figure 2, second line) suggest that the N:Si:P ratios in the Atlantic water at the western entrance of the Strait are lower than the classical Redfield ratio. In the middle of the Strait the N:P ratio is close to the Redfield ratio and Si:P ratio is lower than the Redfield ratio; both of these ratios increase considerably at the eastern entrance of the Strait. The Redfield ratios calculated with the use of the average nutrient concentrations (Figure 2, third line) show that the N:Si:P ratios are close to the Redfield values in the west and middle of the Strait, but they are significantly higher in the east of the Strait. The discrepancies between two calculations can be attributed to the variability in nutrient concentrations affected by physical (upwelling) and biological (phytoplankton consumption) processes along the Eurasian and African coasts of the Strait. Standard errors of the ratios calculated from the individual nutrient measurements show higher variability in values to the east of the Strait than to the west. These variations in the Atlantic water to the east of the Strait are due to the upwelling of intermediate waters and nutrient utilization by phytoplankton.

Table 1. The Overall Performance of Dissolved Oxygen ($\mu\text{mol kg}^{-1}$) and Nutrients Analyses (μM) Based on Laboratory Tests

Constituent	Detection limit	Precision	Accuracy at typical concentration
Oxygen	2.0	0.6	$0.6 \mu\text{mol kg}^{-1}$ at $7.8 \mu\text{mol kg}^{-1}$
Silicate	0.05	0.05	$1.5 \mu\text{M}$ at $100 \mu\text{M}$
Phosphate	0.02	0.02	$0.05 \mu\text{M}$ at $2.0 \mu\text{M}$
Nitrate	0.05	0.05	$0.05 \mu\text{M}$ at $30.0 \mu\text{M}$

Figure 2. The sketch of the two-layers model of water mass exchange through the Strait of Gibraltar with average concentrations of nitrate, silicate and phosphate (in μM , $\pm\text{SD}$, first line), N:Si:P molar ratio ($\pm\text{Standard Error}$) based on the calculation of individual nutrient concentrations (second line) and average nutrient concentrations for each transect (third line), and salinity values used for mixing analysis calculated for each transect as an average for the entire water mass (fourth line). Values of Standard Error in line two are calculated from molar ratio values. Entrainment transports between the Atlantic and Mediterranean waters are shown as W_{TR} ($1\text{Sv} = 10^6 \text{ m}^3 \text{ s}^{-1}$), and nitrate, silicate and phosphate exchanges between these layers as N_{TR} , Si_{TR} and P_{TR} , respectively. The Atlantic and the Mediterranean waters are separated by the interface layer, which is identified by salinity values of 37.0, 37.32 and 37.5 on the western, middle and eastern entrance of the Strait, respectively. The depth of this layer increases from about 130–160 m on the southwest to about 15–20 m on the northeast.

[8] In the surface (Atlantic) water, the decrease in the N:Si ratio from the middle of the Strait to the eastern entrance (1.46 to 0.81, respectively), indicates a higher consumption of silicate relative to nitrate by phytoplankton. Additionally, oxygen over-saturation in the Atlantic water (up to 5%) and phosphate concentration below the detection limit ($<0.02 \mu\text{M}$, data not shown) suggest that despite the short length of the Strait ($\sim 60 \text{ km}$) and a highly dynamic environment (surface currents can reach 3–4 knots), these conditions are favorable for photosynthesis by phytoplankton. The chlorophyll values and microphytoplankton biomass increase from the southwest towards the northeast of the Strait, in agreement with the ascent of the interface layer. The microphytoplankton assemblage in central and eastern parts of the Strait is dominated by diatoms ($>90\%$ of total biomass), and is very different from the phytoplankton assemblage found to the west of the Strait, which has a dominance of dinoflagellates and relatively high concentration of microheterotrophs [Gómez *et al.*, 2000]. Figure 2 shows that in the Gulf of Cádiz, concentrations of silicate are lower (first line) than at Tarifa Narrows and in the Western Alboran Sea. It is well known that the lack of

silicate may, to some extent, determine species succession from a diatom to a flagellate community [Parsons *et al.*, 1984], and finally can be responsible for the differences in the N:Si ratio.

[9] In the deep (Mediterranean) water, the N:Si:P molar ratio exhibits similar behavior to that of the Atlantic water: the ratio decreases from east to west. Close to the eastern entrance of the Strait at a depth of about 300 m, an oxygen minimum and nitrate and phosphate concentration maxima (data not shown) indicate an active mineralization of organic material by bacteria. The Alboran Sea oxygen minimum and nutrient maximum are related to increased productivity in the surface layer associated with upwelling in the northern sector of the Alboran anticyclonic gyre [Packard *et al.*, 1988; Minas *et al.*, 1991]. The regeneration of organic material at this depth in the Western Alboran Sea increases the N:P ratio to values significantly higher ($31.5(\pm 6.0):1$, Figure 2) than those found in the Eastern Mediterranean ($24:1$, [Béthoux *et al.*, 2002]). After mixing in the Strait with the Atlantic water, the Mediterranean water leaves the Strait with a ratio closer to the Redfield ratio (Figure 2). The phytoplankton and bacterial activities significantly increase the N:Si:P ratio in the surface and deep waters at the eastern entrance of the Strait. Data from both the northwestern [Thingstad *et al.*, 1998] and the eastern Mediterranean [Zohary and Roberts, 1998] indicate that the growth rate not only of phytoplankton, but also of heterotrophic bacteria, is phosphorus-limited during stratification.

[10] One physical phenomenon that affects the biology in the Strait is the strong shear between Atlantic and Mediterranean waters in the Camarinal Sill area where the Atlantic water accelerates and entrains the Mediterranean water [Wesson and Gregg, 1994]. In order to estimate the shear from the mass conservation equation applied to the two layers system in the Strait, we used the water transport values obtained during the Gibraltar [Bryden *et al.*, 1994; Bray *et al.*, 1995] and CANIGO [Tsimplis and Bryden, 2000] experiments. There are several different water transport estimates in the Strait of Gibraltar in the literature, however we believe that the estimates from the aforementioned experiments are the most accurate and precise because they are based on a large yearlong data set.

[11] From the difference between inflow and outflow between two layers, we estimated that the entrainment of the Atlantic water at the western entrance of the Strait is 0.15 Sv ($0.84 \text{ Sv} - 0.69 \text{ Sv}$), while the value for the Mediterranean water at the eastern entrance is 0.13 Sv ($0.69 \text{ Sv} - 0.82 \text{ Sv}$; Figure 2). The first value is slightly higher than the 0.1 Sv that has been presented by Wesson and Gregg [1994] to the east of the Camarinal Sill. For the Atlantic water in the west and Mediterranean water in the east, we compared the rate of entrainment with the rate of water transport for each water mass, i.e. 0.15 Sv with 0.84 Sv in the west, and 0.13 Sv with -0.82 Sv on the east, respectively. These results show that 18% of the Atlantic water with ‘low’ N:Si:P ratio re-circulates back to the Atlantic with Mediterranean water and 16% of the Mediterranean water with ‘high’ N:Si:P ratio flows back to the Mediterranean with Atlantic water. The uncertainty of these estimates is associated with the accuracy of the water transport estimates, which according to the CANIGO obser-

Table 2. N, Si and P Values (μM) of the Mediterranean Water (MW) in the Gulf of Cádiz and the Atlantic Surface Water (ASW) in Western Alboran Sea Determined From Two-Point Mixture Calculations

Water masses	Sal	N	ΔN	Si	ΔSi	P	ΔP
MW	37.627	7.7	1.3	6.8	1.9	0.36	0.14
ASW	36.432	4.8	-2.0	3.0	-0.3	0.30	-0.17

ΔN , ΔSi and ΔP are the differences between the average observed values (first line in Figure 2) and those calculated from mixing analysis (in μM).

vations is about 0.06 Sv. This accuracy implies that variations of the entrainment between inflow and outflow can be as high as 40% for the re-circulation of the Atlantic water and 46% for the re-circulation of the Mediterranean water.

[12] We find higher nutrient concentrations in the Atlantic water to the east of the Camarinal Sill than to the west illustrating the input of nutrient constituents due to the mixing between two layers (Figure 2). It is well documented that when mixing events occur at or near the sill region of the Strait, the Atlantic water is enriched with nutrients and advected towards the Mediterranean [e.g., Minas *et al.*, 1991; Echevarria *et al.*, 2002]. Minas and Minas [1995] noted that Mediterranean water induces a hydrological recycling of high N:P water at the sill, back to the Mediterranean. The very high N:P waters (20 to 50) are situated just under the halocline in the Alboran Sea from where they are partly destined to go back to the western Mediterranean basin.

[13] Semidiurnal tidal fluctuations in the Strait can reverse the flows [La Violette and Lacombe, 1988], and the periodic occurrence of nonlinear internal waves can support mixing that increases the N:Si:P ratio in the Atlantic and decreases it in the Mediterranean waters. Nonlinear internal wave packets are generated at the main bathymetric sill (the Camarinal sill) located in the western approaches to the Strait and have been found 200 km inside the Alboran Sea [Pistek and La Violette, 1999].

[14] Additionally, close to Europa Point on Gibraltar there is an upwelling that brings deep waters with ‘high’ N:Si:P ratios to the surface (Figure 2). The upwelling is an almost permanent feature in this area. Two mechanisms have been suggested for the upwelling dynamic in this region: wind stress and the southward drifting of the Atlantic water [Tarek *et al.*, 2000]. Wind-driven upwelling dominates in coastal zones and on the shelf, while upwelling associated with southward drifting of the Atlantic water prevails further offshore. Wind-driven upwelling influences a larger area adjacent to the Strait and lifts water that has a higher nutrient concentration [Tarek *et al.*, 2000].

[15] Mixing analysis has been performed on the mean nutrient values given in Figure 2 (first line). By considering the values at the top left of Figure 2 as the values of ‘pure’ Atlantic water and the values at bottom right for ‘pure’ Mediterranean water and using salinity as a conservative component, we calculated the 2-point mixture values of N, Si and P for the other two water masses at the west and east ends of the Strait, i.e. Mediterranean and Atlantic waters respectively. We first applied the linear mixing equation to the salinity values (see Table 2) in order to derive the percentage of Mediterranean and Atlantic water mixed by physical processes. Using these mixing coefficients, the

values of N, Si and P resulting from physical processes were calculated from the “pure water” values of N, Si, and P (Table 2). The differences between the observed and calculated values quantify to what extent the biological processes affect the water within the Strait. The differences in Table 2 indicate that the nutrient content of the Mediterranean water in Gulf of Cádiz is modified by remineralization, while consumption is affecting the nutrient concentrations of the Atlantic water in the western Alboran Sea. In the Atlantic water the differences between observed values and those from mixing analysis are negative while in the Mediterranean water, concentrations of observed nutrients are lower than those predicted from the mixing model.

[16] Using the vertical and horizontal nutrient fluxes in the Strait (Figure 2), we estimated that in the Atlantic water entering the Mediterranean Sea, physical and biological processes contribute about 16% and 84%, respectively, to the N:Si:P increase. More observations on the mass transport due to upwelling in the area close to Europa Point would help to clarify the contribution of biological processes. The Atlantic water entering the Mediterranean Sea is already depleted of nutrients, especially phosphate, with N:Si:P ratios similar to the deep waters of the Eastern and Western Basins. These observations are in disagreement with the conclusion by Krom *et al.* [1991] that states that the degree of phosphorus limitation in the Mediterranean Sea increases from west to east across the entire basin. The result presented here implies that the role of the Atlantic water in the nutrient balance of the Mediterranean Sea should be reconsidered.

4. Summary

[17] Spatial distribution of nutrients in the Strait of Gibraltar during April 1998 shows that the N:Si:P molar ratios in the Atlantic water entering the Strait (western entrance) are lower than the classical Redfield ratios and increase dramatically along the Strait going from the western to the eastern entrance of the Mediterranean. A similar increase is found for the outflowing Mediterranean waters. The ratios in the surface and deep waters at the eastern entrance of the Strait are similar to those found in the Eastern Mediterranean Basin, thus suggesting that the role of the Atlantic water in the nutrient balance of the Mediterranean Sea should be reconsidered. The biological processes responsible for the observed spatial variability are nutrient consumption by phytoplankton and nutrient regeneration by bacteria in the surface and deep waters at the eastern entrance of the Strait. However physical processes like vertical shear at the interface of the Atlantic and Mediterranean waters, tidal fluctuations and upwelling are identified as the main phenomena affecting the biology in the Strait. Finally, our results indicate that the Strait of Gibraltar area is phosphorus-limited for the growth of phytoplankton and heterotrophic bacteria.

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