Continental Shelf Research 44 (2012) 83–93

Contents lists available at SciVerse ScienceDirect

Continental Shelf Research

journal homepage: www.elsevier.com/locate/csr

Research papers

New insights into C, N and P stoichiometry in the Mediterranean Sea: The Adriatic Sea case

C. Santinelli [a,*], V. Ibello [b], R. Lavezza [a], G. Civitarese [c], A. Seritti [a]

[a] CNR, Consiglio Nazionale delle Ricerche, Istituto di Biofisica, Via Moruzzi, 1, 56124 Pisa, Italy
[b] Middle East Technical University, Institute of Marine Sciences, P.O. Box 28, 33731 Erdemli-Mersin, Turkey
[c] Istituto Nazionale di Oceanografia e di Geofisica Sperimentale (OGS), Borgo Grotta Gigante 42/c, 34010 Sgonico (TS), Italy

ARTICLE INFO

Article history:
Received 23 September 2011
Received in revised form
15 February 2012
Accepted 23 February 2012
Available online 6 March 2012

Keywords:
DOC
DON
DOP
Adriatic Sea
Nutrients
Water masses

ABSTRACT

Vertical distributions of dissolved organic carbon (DOC), nitrogen (DON) and phosphorous (DOP) were studied in the Southern Adriatic basin in two contrasting periods: autumn (high stratification) and winter (high extent of mixing). These data provide the first observations of dissolved organic matter (DOM) stoichiometry in a key area of the Mediterranean Sea.

DOC and DON values are similar to those reported for other areas of the Mediterranean Sea as well as for tropical and temperate regions of the oceans. Surface DOP values are about one order of magnitude lower than those reported for the oceanic waters, confirming the low availability of P in the Mediterranean Sea. Consequently, surface DOM (C:N:P=1189–1411:86–88:1) has higher proportions of C and N with respect to P than in the oceans. DOM stoichiometry in the deep waters of the Southern Adriatic ranged between 993:85:1 and 1693:108:1, indicating a depletion of DOC (or an elevation of DON and DOP) with respect to the old western Mediterranean deep waters. This finding can be explained by the young age of the water masses in the Southern Adriatic, which can mask the effect of mineralization. Our data clearly show that physical processes (water mass circulation, deep water formation and extent of stratification) affect both distribution and stoichiometry of DOM. Finally, we discuss the role of the Adriatic Sea in maintaining the high N:P ratio observed in the Eastern Mediterranean Sea.

1. Introduction

Dissolved organic matter (DOM) is the largest and least understood reservoir of organic carbon on the Earth. Many of the molecules occurring in its pool have not yet been characterized at the molecular level (Benner, 2002; Hansell et al., 2009). From a bulk perspective it comprises three fractions: (1) dissolved organic carbon (DOC), which can give quantitative information on the whole DOM pool; (2) dissolved organic nitrogen (DON); and (3) dissolved organic phosphorous (DOP) (Benner, 2002).

DOM represents the main resource for heterotrophic prokaryotes. Depending on C:N:P ratios, they may also need inorganic N and P. In the oceans, it has been reported that heterotrophic prokaryotes may account for ~40% of the total uptake of inorganic P, N and Fe (Kirchman, 2000). Heterotrophic prokaryotes are the only marine organisms capable of both releasing inorganic nutrients through organic matter mineralization and of using inorganic nutrients in order to balance their N and P needs. Phytoplankton mainly use inorganic nutrients in order to complete photosynthesis while the grazers release inorganic compounds (or organic matter then mineralized by prokaryotes), primarily through excretion and production of faecal pellets. Since the finding of Redfield (1934) that the atomic nitrogen-to-phosphorous ratio (N:P) is 16 both in phytoplankton and in oceanic waters, many attempts have been made to understand whether N:P=16 has a theoretical significance in cells. Recent studies suggest that it has no intrinsic significance, but it is an average value affected by the dominant phytoplankton group as well as by nutrient availability (Loladze and Elser, 2011 and literature therein).

Though DOM stoichiometry drives the key role that DOM plays in marine biogeochemical cycles, currently the main improvement in knowledge is of DOC concentration and distribution, in both the oceans (Hansell, 2002; Hansell et al., 2009; Carlson et al., 2010 and literature therein cited) and the Mediterranean Sea (Santinelli et al., 2010, and literature therein cited). In contrast, information on DON and DOP is still scarce for both the oceans (Loh and Bauer, 2000; Benner 2002; Bronk 2002; Karl and Björkman, 2002; Hopkinson and Vallino, 2005 and literature therein cited) and the Mediterranean Sea (Doval et al., 1999; Raimbault et al., 1999; Moutin and Raimbault, 2002; Lucea et al., 2003; Aminot and Kérouel, 2004; Krom et al., 2005; Pujo-Pay et al., 2011). This is mainly due to their very low

* Corresponding author.
E-mail address: chiara.santinelli@pi.ibf.cnr.it (C. Santinelli).

0278-4343/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.csr.2012.02.015

concentrations and to the limits of the analytical techniques. The errors associated with the calculated ratios are high, leading to highly variable values. In the oceanic surface, DOM stoichiometry ranges are 272–297:22–18:1 in the eastern North Pacific and the Southern Ocean (Loh and Bauer, 2000) and 374:27:1 according to data from the Georges Bank, Middle Atlantic Bight and the Hawaiian Ocean Time Series (HOTS) (Hopkinson and Vallino, 2005). At depth, DOM has higher DOC and DON with respect to DOP, with quoted stoichiometry ranges between C:N:P=408–427:27–37:1 (Loh and Bauer, 2000) and C:N:P=3511:202:1 (Hopkinson and Vallino, 2005).

Recently, a very large set of DOC, DON and DOP data has been reported for a section across the Mediterranean Sea (from the Gulf of Lions to the Levantine basin) (Pujo-Pay et al., 2011). C:N:P ratios show that surface DOM has higher DOC and DON with respect to DOP (1050–1560:84–120:1) in the Mediterranean Sea than in the oceans. In the old deep Mediterranean water, DOM stoichiometry shows values similar to the highest ones reported for deep oceanic waters. It is important to remember that the estimated time for Mediterranean water renewal is about 126 years (Roether and Schlitzer, 1991). As a consequence, the oldest waters of the Mediterranean Sea are at least one order of magnitude younger than oceanic deep waters. In addition, each winter, in areas of deep water formation, there is a movement of surface water to depth which leads to a general increase in both oxygen and DOC (Santinelli et al., 2010). Another peculiar feature of the Mediterranean Sea is its high N:P ratio, increasing from 20 to 25 eastward (Ribera d'Alcalà et al., 2003; Krom et al., 2005; Pujo-Pay et al., 2011).

To our knowledge, no information on DOM stoichiometry has yet been published for the Southern Adriatic. This is a key area because it is the most important site of deep water formation for the Eastern Mediterranean Sea and it is influenced by the input of one of the largest Mediterranean rivers (Po). In addition, it could play an important role in the high N:P ratio observed in the Mediterranean Sea (Ribera d'Alcalà et al., 2003; Civitarese et al., 2005).

In this paper we report the first DOC, DON and DOP data for the Southern Adriatic basin. Their distribution was studied, together with oxygen and inorganic nutrients, during two cruises carried out in the framework of the Italian Project "VECTOR" (VulnErability of the Italian coastal area and marine Ecosystems to Climatic changes and Their rOle in the Mediterranean caRbon cycles). The main goals of this study are: (i) to provide the first information on the DOM pool in the Adriatic Sea in two contrasting periods: winter (high vertical mixing) and autumn (maximum extent of stratification); (ii) to highlight peculiarities of DOM stoichiometry in the Adriatic Sea with respect to the global ocean; (iii) to understand the role of water circulation in shaping DOM concentrations and distributions; and (iv) to provide some insight into the high N:P ratio in the Mediterranean Sea.

2. Materials and methods

2.1. Sampling

The study area and sampling stations are reported in Fig. 1. Stations were located in the Southern Adriatic basin along a section at 41°–43°N and 17°–19°E, crossing the Southern Adriatic Pit.

Seawater was collected with a CTD – rosette equipped with Niskin bottles, at the following depths: 0, 10, 25, 50, 75, 100, 150, 200, 250, 300, 400, 500, 600, 700, 800, 900, 1000 and 1100 m, and few meters above the bottom, at each station. Samples were collected in September 2007 and in January 2008.

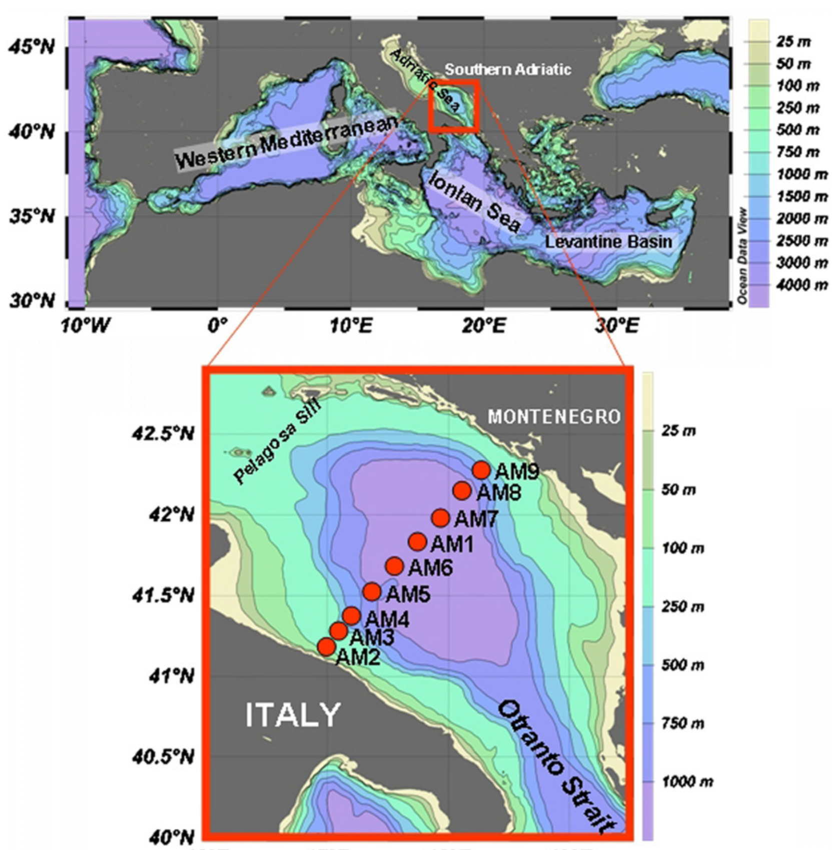

Fig. 1. Study area and sampling stations during the two cruises.

At all stations, pressure, conductivity and temperature were measured with an SBE 911 plus CTD, equipped with a rosette sampler with 12×10 L Niskin bottles. Physical data were kindly provided by the "Istituto Nazionale di Oceanografia e Geofisica Sperimentale" (OGS), Trieste (V. Cardin). CTD data have been published in Cardin et al. (2011).

2.2. Dissolved oxygen

Dissolved oxygen (DO) was sampled in specific oxygen glass bottles and determined by means of a Metrohm automatic burette following the Winkler procedure (Carpenter, 1965). The final point was determined automatically by means of a redox electrode. The coefficient of variation was 0.04% with a range of 0.01 to 0.10%.

2.3. Organic and inorganic nutrients

Seawater for nutrient measurements was collected into 20-ml high density polyethylene (HDPE) bottles soaked overnight in cloridric acid and rinsed with water sample before its collection. Samples were stored at $-20\,^{\circ}$C until analysis. The analyses of inorganic nutrients were carried out using a hybrid autoanalyzer equipped with a Chemlab flow colorimeter, following the procedure described by Grasshoff et al. (1983) with some modifications. For P, this method measures the operationally defined pool of soluble reactive P (SRP) (Karl and Björkman, 2002). The coefficient of variation was 0.04% with a range of 0.01 to 0.10%. The detection limit (DL) was 0.02 μM for nitrate (DIN) and 0.01 μM for SRP.

Samples for total dissolved phosphorous (TDP) and nitrogen (TDN) were filtered on precombusted (450 °C, 6 h) GF/F filters before storage. Laboratory analyses were carried out by a photo-oxidation (UV) method using an irradiation unit (Thalassia mod. RFC 239) equipped with a high-energy 900 W UV lamp (Heareus TQ 1200). The methods have been slightly modified from the procedures reported by Walsh (1989) for TDN and by Armstrong et al. (1966) for TDP. Both dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) were calculated by difference (DON=TDN−DIN and DOP=TDP−SRP). This method could underestimate DOP because SRP may include some organic P.

The coefficient of variation on a set of different concentration replicates was 9.9% (4.3–16.2%) for DON and 13.3% (11.4–14.9%) for DOP.

The average variance (σ^2) of element ratios ($R=x{:}y$) was calculated from the equation usually applied to calculate the propagation of errors (Bevington and Robinson, 1992):

$$\sigma_R^2 = \frac{y^2}{x^2}\left(\frac{\sigma_x^2}{x^2} + \frac{\sigma_y^2}{y^2}\right)$$

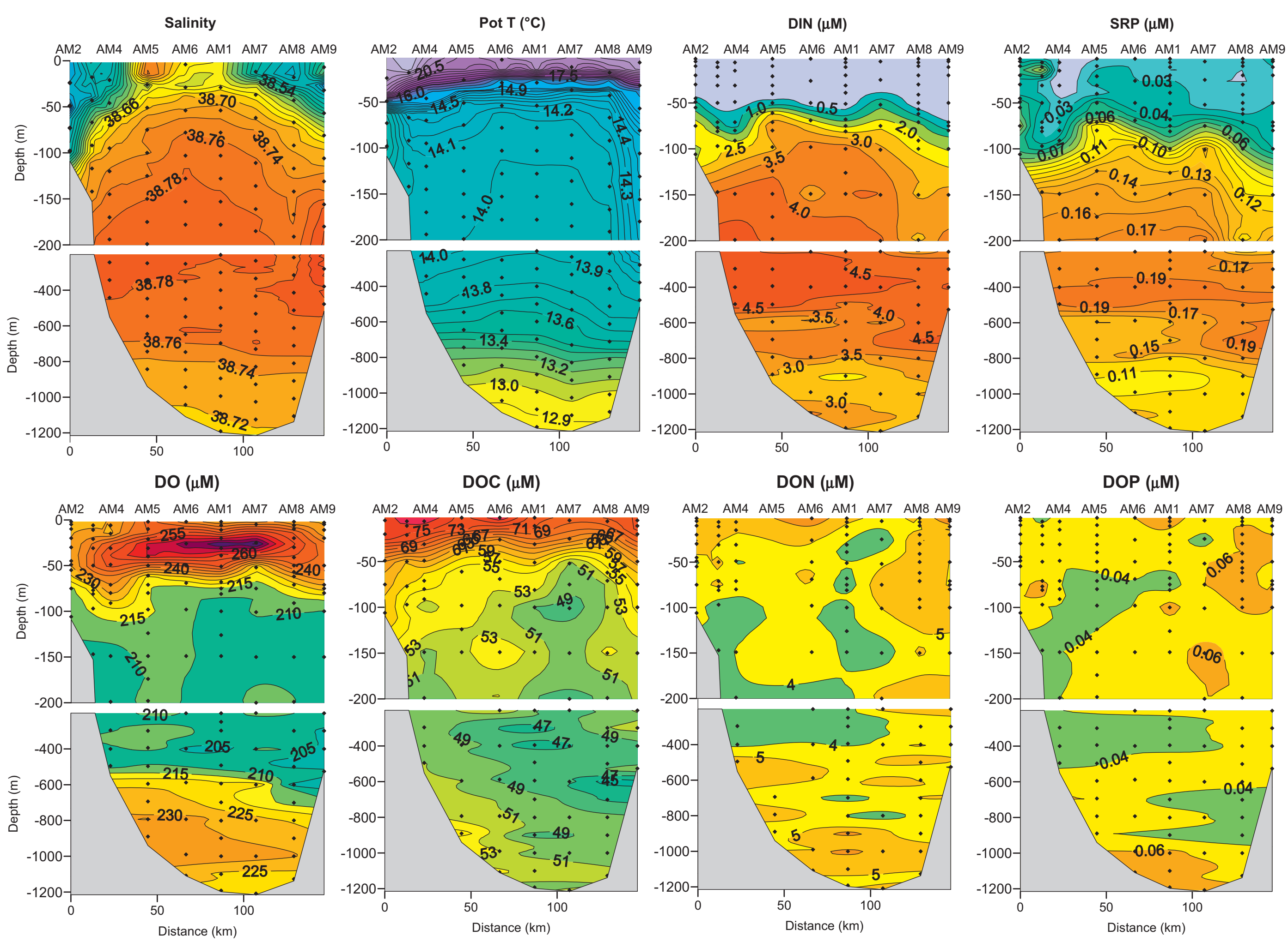

Fig. 2. Vertical distribution of physical (salinity; Pot T: potential temperature) and biogeochemical parameters (DIN: nitrate; SRP: soluble reactive phosphorous; DO: dissolved oxygen; DOC: dissolved organic carbon, DON: dissolved organic nitrogen; DOP: dissolved organic phosphorous) in September 2007.

x and y are the two variables independently measured and σ^2 is the variance of the variables. The average relative standard deviations were 5% for DOC:DON and 20% for both DOC:DOP and DON:DOP. These values are in agreement with those reported by Aminot and Kérouel (2004) calculated with the same method.

2.4. Dissolved organic carbon (DOC)

DOC samples were filtered, immediately after collection, through a 0.2-μm membrane filter (Sartorius, Minisart, SM 16534) under extra pure Nitrogen pressure and stored at 4 °C in the dark until analysis (within 3 months). DOC samples were analyzed by means a Shimadzu TOC-Vcsn. Samples were acidified with 2 N HCl and sparged for 3 min with CO_2-free pure air, in order to remove inorganic carbon before the high temperature catalytic oxidation. One hundred microliters of sample was injected into the furnace after a four-fold syringe washing. From 3 to 5 replicate injections were performed until the analytical precision was within $<2\%$ (± 1 μM). The calibration curve was performed by using four different solutions of potassium phthalate, in the same concentration range as the samples. The reliability of the measurements was checked daily by using consensus reference materials (CRM) kindly supplied by Prof. D.A. Hansell, University of Miami. At least two CRM and two low carbon water (LCW) analyses were performed for each analytical day (measured value = nominal value $\pm$ 0.5 μM). For further analytical details see Santinelli et al. (2010).

3. Results

3.1. Vertical distributions of C, N and P in winter and autumn

The vertical distributions of DOC, DON and DOP were studied in September 2007 (Fig. 2) and January 2008 (Fig. 3), along the whole section (Fig. 1), together with the vertical distributions of salinity, potential temperature, DO, DIN and SRP.

Overall, DOC, DON and DOP ranged between 45 and 79 μM, 1.8 and 7.2 μM, and 0.02 and 0.08 μM, respectively.

3.1.1. Surface layer (0–200 m)

In the upper 200 m, interesting differences were observed in the vertical distributions of DOC, DON and DOP between the two periods. In September 2007 (Fig. 2), the waters above the thermocline (at ~50 m) were characterized by a maximum in DOC (>62 μM) and relatively high values of both DON (>5 μM) and DOP (>0.05 μM), while they were almost completely devoid of DIN (<0.5 μM) and SRP (<0.03 μM). Two veins of fresher water ($S<38.54$) were observed close to the coasts, representing clear signals of the northward East Adriatic Current (EAC) along the eastern side of the section, and the southward West Adriatic Current (WAC) along the Italian slope (Falco et al., 2000; Poulain, 2001).

In January 2008 (Fig. 3), the high extent of vertical mixing (down to 600 m as visible in the salinity and potential temperature vertical distribution) led to a homogenization of the chemical

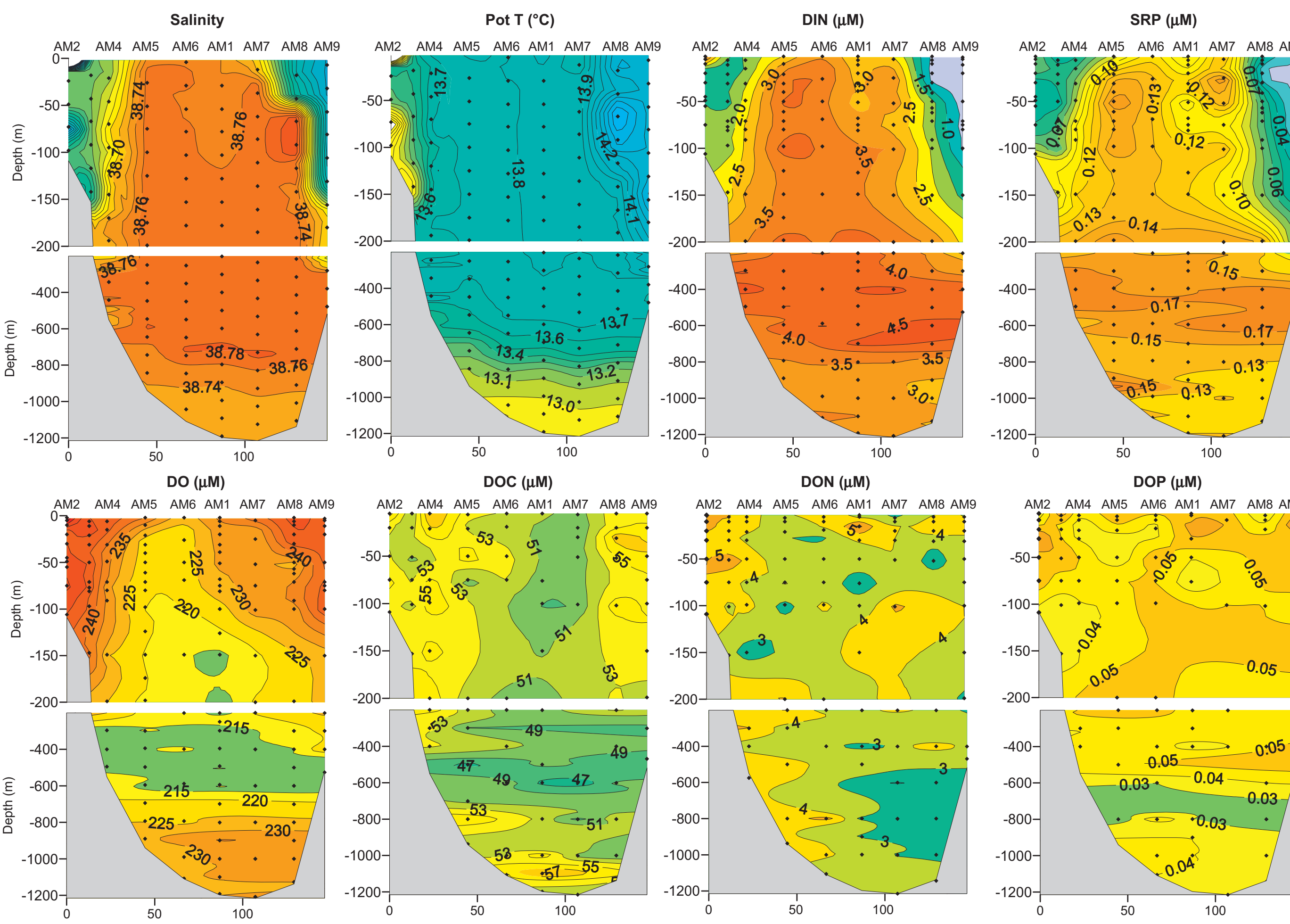

Fig. 3. Vertical distribution of physical and biogeochemical parameters in January 2008. For abbreviations look at the caption of figure 2.

properties. The upper 200 m of the central stations (AM5–AM7) were characterized by a decrease in both DO (< 240 μM) and DOC (< 53 μM), and by an increase in DIN (> 3 μM) and SRP (> 0.10 μM), with respect to September 2007. No clear patterns were found in DON (2–5 μM) and DOP (0.03–0.06 μM) distributions. The occurrence of the EAC and WAC was also observed in January 2008 (Fig. 3). The EAC, occurring in the upper 150 m at stations AM8 and AM9, was characterized by a temperature higher than 14.2 °C, low nutrients (DIN < 2 μM, SRP < 0.05 μM), and high DO (232–250 μM) and DOC (54–57 μM) concentrations. The WAC, occurring in the upper 150 m of the stations AM2–AM4, was characterized by a temperature lower than 13.3 °C, low DIN (< 2 μM) and SRP (< 0.07 μM), and high DO (235–255 μM), DOC (54–58 μM) and DON (4–7 μM) values.

3.1.2. Intermediate layer

The intermediate layer (150–450 m) was mainly occupied by Levantine Intermediate Water (LIW) in September 2007. This water mass can be clearly recognized by its salinity maximum (> 38.77) (Fig. 2). In January 2008, the convective mixing, which extended from 0 to about 600 m, hindered clear identification of the core of LIW. In both periods, the maximum values of DIN (4.5–5.0 μM) and SRP (0.15–0.19 μM) and the minimum of DO (205 μM) and DOC (44–49 μM) occurred in the layer 200–500 m, immediately below the salinity maximum (LIW core). This finding is probably due to the northward advection of a vein of the transitional Eastern Mediterranean Deep Water (tEMDW). This is the oldest water mass occurring in the Eastern Mediterranean Sea; it is located at about 500–1500 m and it is characterized by oxygen and DOC minima (Seritti et al., 2003; Manca et al., 2006) and nutrient maxima. In January 2008, minima of DOC, DON and DOP were found close to the eastern side of the section below 500 m (Fig. 3). This finding could be related to the deep convection that pushed the tEMDW core to the bottom of the mixing layer.

3.1.3. Deep layer

In September 2007, ventilated deep waters (DO = 230–234 μM) occurred below 800 m. The DO maximum was observed close to the western flank of the pit. A slight increase in DOC (up to 56 μM) was found in correspondence with this oxygenated water. It is noteworthy that the Adriatic dense Deep Water (AdDW) was also characterized by high values of both DON (5–6 μM) and DOP (> 0.06 μM) and that the intrusion of this water led to a decrease in DIN (< 3 μM) and SRP (< 0.12 μM) (Fig. 2).

In January 2008 the waters below 800 m were still ventilated, with DO concentrations (DO = 230–236 μM) similar to those found in September 2007. In contrast, the DO maximum occurred at the eastern part of the pit. In this layer an increase in DOC was observed (to 58–60 μM) below 1000 m at station AM1. In correspondence with this oxygenated water, low values of both organic and inorganic N and P were observed (DIN < 3 μM; SRP < 0.13 μM; DON = 2–3 μM; DOP = 0.02–0.05 μM), while DON and DOP showed high values close to the Italian coast (DON = 4–6 μM; DOP = 0.06–0.08 μM) (Fig. 3).

3.2. N:P ratio and DOM stoichiometry

Table 1 summarizes the main physical and chemical properties of each water mass identified in the study area in both periods. The DOC:DON:DOP ratios in the water masses were calculated as averages of the ratios calculated for the samples collected in each water mass (Table 2). The significance of the difference between the average values of each parameter was tested using two-tailed *t*-test. The probabilities, calculated from the *t*-test, are reported for the differences between the same water mass in the two periods and between the water masses in each period (Table 3).

Table 1
Average value ± standard deviation and range of the chemical properties (DO: dissolved oxygen; AOU: apparent oxygen utilization; DIN: nitrate; SRP: soluble reactive phosphorous; TDN: total dissolved nitrogen; TDP: total dissolved phosphorous; N_{DO}, N_{DIN}, N_{SRP}: number of samples for DO, DIN and SRP, respectively; DOC: dissolved organic carbon; DON: dissolved organic nitrogen; DOP: dissolved organic phosphorous) in each water mass (WM) identified in the two periods (SW: surface water; LIW: Levantine intermediate water; AdDW: Adriatic dense Deep Water). The physical characteristics and the depth of each water mass are also reported (S: salinity; θ: potential temperature; σ_θ: potential density).

Cruise	WM	Depth (m)	S	θ (°C)	σ_θ (Kg m^{-3})	DO (μM)	AOU (μM)	DIN (μM)	SRP (μM)	TDN (μM)	TDP (μM)	N_{DO}, N_{DIN}, N_{SRP}	DOC (μM)	DON (μM)	DOP (μM)
September 2007	SW	2–75	38.40–38.77	14.1–23.0	26.60–28.88	242 ± 17	–	0.17 ± 0.3	0.03 ± 0.02	4.7 ± 0.8	0.08 ± 0.02	40, 29, 46	70 ± 7	4.6 ± 0.9	0.05 ± 0.01
						225–285		0.01–1.47	0.01–0.11	2.5–6.9	0.05–0.20		57–79	2.5–6.9	0.03–0.07
	LIW	150–530	38.78–38.82	13.8–14.1	29.10–29.16	208 ± 4	46 ± 4	4.4 ± 0.4	0.18 ± 0.02	8.2 ± 0.7	0.23 ± 0.02	23, 24, 24	49 ± 2	3.7 ± 0.7	0.04 ± 0.01
						202–216	38–53	3.1–4.9	0.14–0.21	7.2–9.8	0.20–0.26		45–54	2.8–5.2	0.02–0.06
	AdDW	800–bottom	38.72–38.74	12.9–13.2	29.25–29.30	229 ± 4	29 ± 4	3.0 ± 0.4	0.12 ± 0.02	7.3 ± 1.2	0.17 ± 0.02	15, 15, 15	51 ± 2	4.6 ± 0.8	0.06 ± 0.01
						222–235	24–37	2.2–3.9	0.09–0.16	4.2–9.2	0.11–0.21		47–56	3.4–6.2	0.03–0.08
January 2008	SW	2–200	37.77–38.77	11.1–14.6	28.76–29.15	239 ± 11	–	2.0 ± 1.2	0.08 ± 0.04	6.2 ± 1.5	0.12 ± 0.04	57, 57, 57	53 ± 3	4.1 ± 1.0	0.05 ± 0.01
						214–270		0.2–4.0	0.02–0.16	3.4–9.7	0.05–0.22		49–59	2.3–7.2	0.02–0.08
	LIW	200–600	38.77–38.78	13.6–13.8	29.14–29.19	214 ± 3	41 ± 3	4.3 ± 0.2	0.17 ± 0.01	7.8 ± 1.1	0.21 ± 0.02	19, 19, 19	50 ± 2	3.7 ± 1.0	0.05 ± 0.01
						210–221	33–45	3.8–4.8	0.14–0.19	5.4–9.6	0.19–0.26		45–54	1.8–5.3	0.03–0.06
	AdDW	800–bottom	38.73–38.74	12.9–13.1	29.27–29.30	230 ± 4	29 ± 4	3.3 ± 0.2	0.13 ± 0.02	6.8 ± 0.8	0.2 ± 0.02	12, 12, 12	54 ± 3	3.5 ± 0.6	0.03 ± 0.01
						224–236	22–35	2.8–3.6	0.11–0.20	5.7–7.9	0.14–0.20		50–60	2.9–4.6	0.02–0.04

Table 2
DOC, DON and DOP values and their ratio reported in the literature for the Mediterranean Sea. Data from different locations in the oceans are also indicated for comparison. The values observed in this study are reported as the average ± standard deviation of the ratio for each sample collected in the water masses during both cruises (see Table 1).

Area	Depth (m)	DOC (μM)	DON (μM)	DOP (μM)	DOC:DON	DOC:DOP	DON:DOP	Reference
Ocean (Eastern North Pacific and Southern Ocean)	Surface layer (0–100 m)	50–72	2.9–4.5	0.15–0.23	11–17	222–338	17–27	Loh and Bauer (2000)
	Deep water (> 1000 m)	35–46	1.7–4.4	0.06–0.17	9–16	237–688	16–44	
Ocean (North Pacific subtropical Gyre)	0–175 m	63–105	3.7–6.2	0.10–0.27	14.8–16.4	390–483	24.0–31.4	Church et al. (2002)
Ocean (Georges Bank, Middle Atlantic Bight and HOTS)	Surface layer (0–100 m)	30–160	1–11	0.00–0.45	14	374	27	Hopkinson and Vallino (2005)
	Deep water (> 1000 m)				17	3511	202	
Off North of Spain	Surface layer	65–75	4–5	–	15–16	–	–	Doval et al. (1999)
	100–1500 m	46–51	2.9	–	16–17	–	–	
Gulf of Lions	Surface layer	67–69	4–4.2	0.08	17	920–970	55–57	Aminot and Kérouel (2004)
	200–600 m	46–48	3.0	0.04	15–16	1100–1200	70–76	
	800–1500 m	46	2.7	0.03–0.04	17	1100–1800	64–1062	
Gulf of Lions	Surface layer (0–160 m)	60–100	4.5–5.5	n.d. – 0.1	13–18	600–10000	45–55	Raimbault et al. (1999)
North West Med	Surface layer (0–100 m)	80–120	5–6	n.d.	16–20	–	–	Lucea et al. (2003)
	200–500 m	40–60	1–6	n.d.	10–40	–	–	
	600–bottom (1000 m)	50–80	1–5	n.d.	50–16	–	–	
West Med	0–100 m	–	4.6 ± 0.6	0.08 ± 0.02	–	–	57	Moutin and Raimbault (2002)
	300–500 m	–	3.1 ± 0.3	0.06 ± 0.01	–	–	52	
	> 1000 m	–	2.8 ± 0.1	0.03 ± 0.02	–	–	93	
East Med	0–100 m	–	4.5 ± 0.6	0.06 ± 0.03	–	–	75	
	300–500 m	–	3.7 ± 0.4	0.05 ± 0.02	–	–	74	
	> 1000 m	–	3.3 ± 0.3	0.05 ± 0.02	–	–	66	
West Med	0–100 m	50–68[a]	4.1–5.5[a]	0.03–0.06[a]	12.5[b]	1050[b]	84[b]	Pujo-Pay et al. (2011)
	200–800 m	38–41[a]	2.5–4.0[a]	–	12.4[b]	3100[b]	250[b]	
	1000–2900 m	38–42[a]	2.9–4.3[a]	–	12.5[b]	5000[b]	400[b]	
East Med	0–100 m	56–72[a]	3.5–6.3[a]	0.01–0.10[a]	13.0[b]	1560[b]	120[b]	
	200–800 m	37–50[a]	3.0–4.0[a]	–	12.4[b]	3100[b]	250[b]	
	1000–3000 m	38–41[a]	3.0–3.5[a]	–	12.1[b]	3150[b]	260[b]	
South East Levantine Basin	Photic zone	65–100	3–11	0.05	9–21	1300–2000	60–220	Krom et al. (2005)
	500–1200	40–60	1–2	0.04	40–30	1000–1500	25–50	
Otranto Strait	0–200	–	4–6[c]	0.02–0.06[c]	–	–	100–200	Civitarese et al. (1998)
	200–1200	–	5–7[c]	0.04–0.08[c]	–	–	87–125	
Southern Adriatic September 2007	Surface layer (0–200 m)	57–79	2.5–6.9	0.03–0.07	16 ± 3	1411 ± 343	86 ± 16	This study
	LIW (200–600 m)	45–54	2.8–5.2	0.02–0.06	13 ± 2	1279 ± 396	97 ± 32	
	ADW (800–bottom)	47–56	3.4–6.2	0.03–0.08	11 ± 2	993 ± 326	85 ± 22	
Southern Adriatic basin January 2008	Surface layer (0–200 m)	49–59	2.3–7.2	0.02–0.08	14 ± 3	1189 ± 333	88 ± 26	
	LIW (200–600 m)	45–54	1.8–5.3	0.03–0.06	14 ± 4	1107 ± 265	83 ± 15	
	ADW (800–bottom)	50–60	2.9–4.6	0.02–0.04	15 ± 2	1693 ± 566	108 ± 46	

[a] These values were obtained from their figure 5.
[b] These values were obtained from their figure 9.
[c] These values were calculated subtracting DIN and DIP by TDN and TDP data reported by the authors.

Table 3
Probability, calculated with *t*-test (two-tailed), that the difference between average concentrations of DOC, DON and DOP is not significant. Probabilities were tested comparing the same water masses [surface (SW), Levantine Intermediate Water (LIW) and Adriatic Dense Water (AdDW)] between September 2007 and January 2008 and the different water masses in each period. The numbers in brackets indicate the number of samples used for the test.

t-test (two tails)			DOC	DON	DOP
September 2007 vs. January 2008	SW	SW	0.000 (27, 40)	0.013 (41, 55)	0.095 (36, 47)
	LIW	LIW	0.938 (20, 15)	0.692 (20, 16)	0.354 (18, 15)
	AdDW	AdDW	0.025 (17, 11)	0.002 (14, 10)	0.001 (13, 8)
September 2007	SW	LIW	0.000 (27, 20)	0.000 (41, 20)	0.000 (36, 18)
	SW	AdDW	0.000 (27, 17)	0.804 (41, 14)	0.554 (36, 13)
	LIW	AdDW	0.023 (20, 17)	0.002 (20, 14)	0.003 (18, 13)
January 2008	SW	LIW	0.000 (40, 15)	0.150 (55, 16)	0.208 (47, 15)
	SW	AdDW	0.868 (40, 11)	0.098 (55, 10)	0.003 (47, 8)
	LIW	AdDW	0.002 (15, 11)	0.695 (16, 10)	0.031 (15, 8)

In the surface water, average concentrations of DOC and DON were significantly different in the two periods (Table 3). In winter, DOM was lower in DOC than in the autumn and the DOC:DON and DOC:DOP average ratios decreased from 16 to 14 and from 1411 to 1189, respectively.

In both periods, LIW was characterized by minima of DOC (Table 1), with a C:N:P ratio of 1279:97:1 in autumn and of 1107:83:1 in winter (Table 2). In autumn, LIW values of DOC, DON and DOP were significantly different from those found in the surface waters and in the AdDW, as a result of the high extent of stratification, while in winter the deep mixing weakened these differences for DON and DOP in particular (Table 3).

The AdDW in September 2007 and January 2008 displayed significant differences in DOM (Tables 1 and 3), even though the high content of DO underlines important contributions of surface waters in both periods. The main feature was a general decrease in DON and DOP and an increase in DOC from autumn to winter, leading to a DOM stoichiometry of 993:85:1 in September 2007 and 1693:108:1 in January 2008.

4. Discussion

4.1. DOC, DON and DOP in the Southern Adriatic and in the oceans

The data reported here show that the DOC and DON values, and their ratios, are similar to those previously reported for the Mediterranean Sea as well as for tropical and temperate regions of the oceans (Table 2). DOP values are in agreement with previous observations in the Mediterranean Sea, and they are about one order of magnitude lower than those reported for the oceans. In addition, DOC:DOP ratios are about three times higher than the oceanic ones (Table 2). This finding is in agreement with the low concentration of P, in both its organic and inorganic forms, in the Mediterranean Sea (Moutin and Raimbault, 2002). It is also important to consider that DOP could be overestimated due to the use of GF/F filters, which do not retain all the particulate matter; in particular, in oligothrophic waters some bacteria with high P:N or P:C ratios may pass through the filter. This further strengthens the observation of lower P in DOM. In both the AdDW and LIW, DOM stoichiometry has lower DOC (or higher DON and DOP) compared to DOM in the old deep Mediterranean and refractory DOM (Hopkinson and Vallino, 2005), while it has lower DOP than the deep water of the eastern North Pacific and the Southern Ocean (Loh and Bauer, 2000). In addition, no correlation was observed between DOC, DON and DOP data collected at different depths in the Southern Adriatic, unlike what was observed in other areas of the Mediterranean Sea (Pujo-Pay et al., 2011) and in the oceans (Hopkinson et al., 1997; Hopkinson and Vallino, 2005). These observations may be explained by (i) the intense vertical mixing, (ii) the young age of the water masses, (iii) the influence of the input from the land, or by any combination of these processes.

It is also interesting to observe that (i) TDN and TDP values were higher in the intermediate layer than below 600–800 m, in particular in September 2007 (Fig. 4), and (ii) TDN and TDP values (Table 1) were markedly lower in both the LIW and AdDW than in deep oceanic waters (TDN$=33.1\pm9.1$ μM; Bronk, 2002; TDP$=1.0$–1.6 μM; Karl and Björkman, 2002). In addition, below 200 m DON was 40–60% of TDN and DOP was 20–40% of TDP (Fig. 4), while they were, respectively, only 10% of TDN (Bronk, 2002) and TDP (Karl and Björkman, 2002) in the deep oceanic waters. These features indicate that though the Mediterranean waters have lower N and P, a higher percentage of TDN and TDP is represented by DOM than in the oceans. This finding could be explained by the young age of Mediterranean waters, which precludes marked TDN and TDP accumulation due to

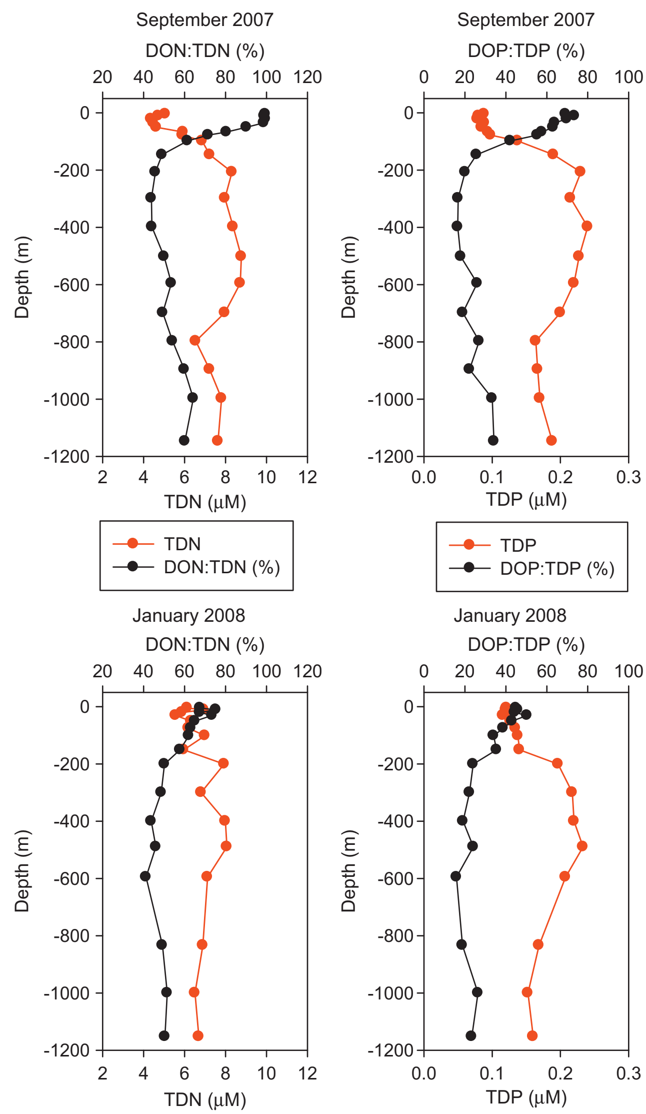

Fig. 4. Average profiles of TDN, TDP, DON:TDN (%) and DOP:TDP (%) in September 2007 and January 2008. The standard deviation ranges were 0.4–1.6 μM and 0.005–0.04 μM for TDN and TDP, respectively. The standard deviations for DON:TDN and DOP:TDP were 0.6–17% in September 2007, and 11–23% in the upper 100 m and 0.4–9% below 200 m in January 2008.

mineralization processes. This observation is confirmed by the values of AOU that in the Southern Adriatic are two- to four-fold lower (22–53 μM) (Table 1) than those reported for oceanic waters (50–200 μM) (Hayase and Shinozuka, 1995; Doval and Hansell, 2000; Arístegui et al., 2002). A similar partitioning between organic and inorganic N and P has been observed comparing deep Atlantic and Pacific oceans. In the older Pacific waters inorganic nutrients have a markedly higher concentration than in the Atlantic ones (Millero and Sohn, 1992).

A similar explanation can be found for TDN and TDP observed in the intermediate and deep waters, whose values were lower than those found in the Otranto Strait in May 1995 (TDN$=$5–12 μM, TDP$=$0.10–0.30 μM) (Civitarese et al., 1998). According to recent findings concerning the decadal variability in the oceanographic properties of the Southern Adriatic, induced by the bimodal oscillation of the Adriatic–Ionian system (Civitarese et al., 2010; Gačič et al., 2010), in 1994–95 the Southern Adriatic was characterized by a period of reduced (or absent) vertical convective mixing (Civitarese and Gačič, 2001). In this period the stabilization of the water column avoided mixing with surface water, characterized by a high content of DO and a minimum of nutrients (Civitarese et al., 1998; Civitarese and Gačič, 2001); as a consequence, mineralization processes produced a net increase in nutrient levels (as well as a decrease in oxygen) in the deep waters (Table 2). On the other hand, during 2007–08 the Southern Adriatic was more saline, thus more active in terms of convective mixing. This may explain the general decrease in nutrients as well as the 20-μM increase in DO concentration.

4.2. *Influence of physical processes (water mass circulation) on DOM distribution and stoichiometry*

The data reported here indicate a clear influence of water mass circulation and stratification on DOM distribution and nutrient ratios. The high stratification occurring at the end of the summer was responsible for trapping DOM in the upper layer, where DOC, DON and DOP showed their highest values. DOM accumulated in the mixed layer was higher in carbon, as already observed in the oceans (Church et al., 2002). In contrast, the extensive mixing in winter led to the dilution of surface waters with the DOM-depleted intermediate waters.

In both periods, minima in DOC, DON and DOP as well as maxima in DIN and SRP were observed in the intermediate layer, occupied by LIW and tEMDW. These water masses were characterized by an oxygen minimum and TDN and TDP maxima, indicating a high extent of mineralization of both POM and DOM (Table 1).

DO distribution clearly shows that the waters below 800 m were well oxygenated in both periods (Figs. 2 and 3 and Table 1). This feature indicates that they had recently been in contact with the atmosphere and that they were younger than LIW and tEMDW. Though these patterns were observed in both months, some differences in DOM stoichiometry were apparent, with a rise in DOC in January 2008. This finding can be explained by the occurrence of a higher fraction of terrestrial DOM in winter than in autumn, as DOM in riverine systems has a C:N ratio of 26 (Bronk, 2002).

As reported above, the Southern Adriatic is characterized by water masses with different oxygen concentrations as result of the extent of mineralization. If we consider the different water masses as the same water collected at different times, we can gain information about mineralization processes from the relationship between the chemical properties.

From all the data collected in the two periods, a linear relationship was found between DO and TDN [slope $= -6.1 \pm 0.5$; $r^2 = 0.38$; $p < 0.0001$] and between DO and TDP [slope $= -197 \pm 13$; $r^2 = 0.50$; $p < 0.0001$]. This finding suggests that the progress of mineralization leads to an increase in both TDN and TDP. The relationships between DIN and SRP (excluding the samples with DIN < 0.1 μM; Fig. 5a) and between TDN and TDP (Fig. 5b) were characterized by slopes of 23.2 and 23.5 respectively. These values are in agreement with previous observations in the Mediterranean Sea (Ribera d'Alcalà et al., 2003; Krom et al., 2005) and indicate that mineralization occurs with high N:P ratios. In order to assess the contribution of DOM mineralization to DIN and SRP regeneration, the correlations TDN vs. DIN and TDP vs. SRP were also studied (Fig. 6). The TDN vs. DIN slope was 0.76 (excluding the samples with DIN < 0.1 μM; Fig. 6a) while the TDP vs. SRP slope was 0.90 (Fig. 6b). These data suggest that unit increases in DIN and SRP correspond to increases of 0.76 and 0.90 in TDN and TDP, respectively. Therefore, the increase in TDN is about 24% less than that of DIN and the increase in TDP is about 10% less than that of SRP, indicating that the decomposition of DOM is responsible for the 24% and 10% increases in DIN and SRP. An external input of dissolved nutrients (such as for example from POM mineralization, atmosphere or rivers) is necessary to observe the increases in both inorganic and total nutrients. In other words, the only explanation of an increase in

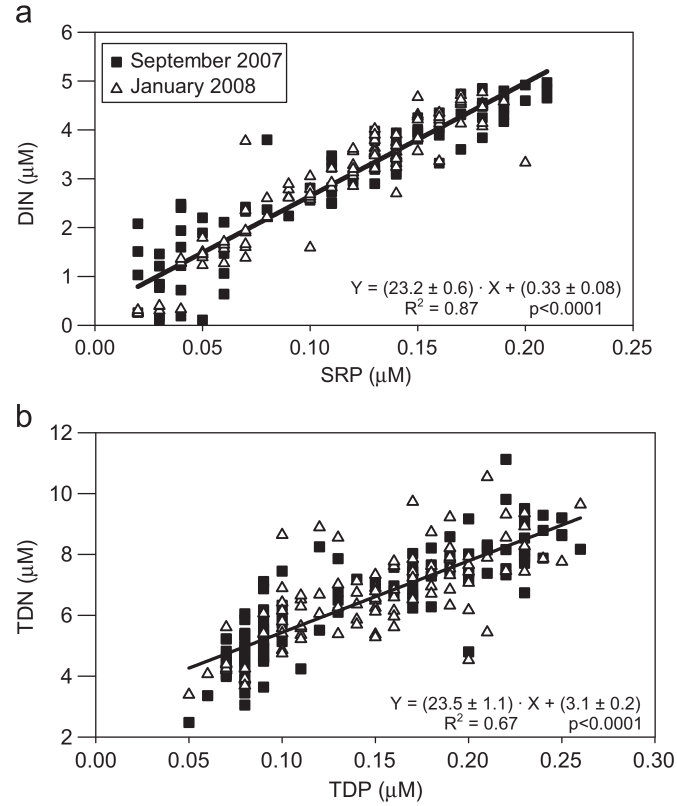

Fig. 5. DIN vs. SRP (a) and TDN vs. TDP (b) relationship in both September 2007 (black squares) and January 2008 (white triangles).

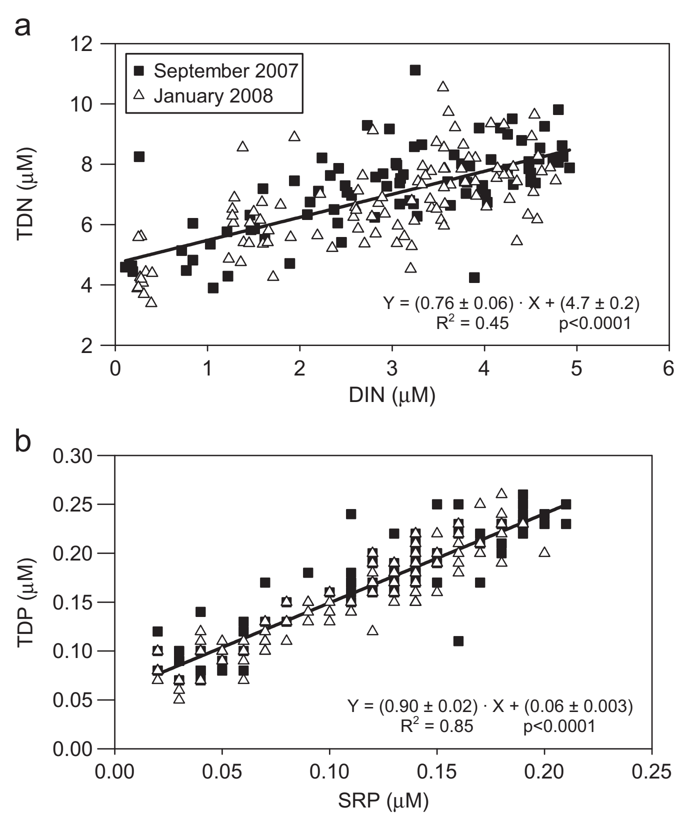

Fig. 6. TDN vs. DIN (a) and TDP vs. SRP (b) relationship in September 2007 and January 2008.

the inorganic nutrients without a corresponding increase in total nutrients is that there is a change in the dissolved pool from organic to inorganic. All the other processes would also increase TDN and TDP. It is surprising that the percentages reported above are exactly the same as those found in a highly productive continental shelf region off the northeastern USA (Hopkinson et al., 1997). Our data show that the processes driving DOM and nutrient dynamics are the same in the Mediterranean Sea as in oceanic waters, despite the strong difference in the temporal scales. This finding supports the idea that the high DOM mineralization rate reported for the Mediterranean Sea allows mineralization of the entire semi-labile fraction in a time one order of magnitude shorter than in the oceans (Santinelli et al., 2010).

4.3. A possible explanation of the high N:P ratio in the Southern Adriatic

One of the most intriguing features of the Mediterranean Sea is the high N:P ratio in the inorganic nutrient pool (Ribera d'Alcalà et al., 2003; Krom et al., 2005; Pujo-Pay et al., 2011). Different processes have been invoked to explain the deviation from the value of 16 proposed by Redfield (1934) for oceanic waters. The unusual Mediterranean nutrient ratio could be due to high N:P values in all the external nutrient inputs to the Mediterranean Sea, especially the atmospheric deposition which represents the major external source of bioavailable N to the eastern basin (Krom et al., 2010). The other hypothesis invokes high rates of nitrogen fixation by seagrasses and N-fixing phytoplankton (Pantoja et al., 2002; Bonnet et al., 2011). A possible role of the water flowing out of the Adriatic Sea has also been hypothesized to support the N:P anomaly (Civitarese et al., 1998). However, even though there is agreement on the high N:P ratio of the sources (nitrogen fixation and/or atmospheric inputs and/or other sources), the specific mechanism by which the high N:P ratio is transferred to the deep layers has not yet been much explored. Recent considerations reported in the literature (Klausmeier et al., 2004; Arrigo, 2005; Weber and Deutsch, 2010; Loladze and Elser, 2011;) led us to re-evaluate the mediterranean N:P ratio taking into consideration organic matter dynamics and the role of the micro-organisms in regulating element fluxes (Fig. 7).

Klausmeier et al. (2004), using an optimization model, showed that the N:P ratio observed in nature is an average value that reflects the diverse phytoplankton assemblage growing under a variety of different environmental conditions. Phytoplankton assemblages with different survival strategies are characterized by different intracellular N:P ratios. In agreement with this model, Weber and Deutsch (2010) observed that the variations in N:P ratio across latitude in Southern Ocean surface waters were governed by regional differences in the species composition of the plankton community. We assume that the N:P ratio in the environment reflects the average N:P in the diverse phytoplankton assemblage (Klausmeier et al., 2004) and that bacteria will consume or mineralize inorganic N and P depending on the C:N:P in DOM and in the bacterial biomass (Kirchman, 2000). In the Southern Adriatic, picophytoplankton dominates the primary producers, representing 96% of the total abundance and 49% of the total biomass, with a strong predominance of Synechococcus (Cerino et al., in press). The C:N:P elemental molar ratios in Synechoccus are 130–165:24–33:1 in nutrient-replete conditions and they increase to 723–779:97–109:1 in P-limited conditions (Bertilsson et al., 2003). Therefore, according to Klausmeier et al. (2004), in an area dominated by Synechoccus with intracellular N:P ratios varying between 24 and 110, the N:P ratio in the external inorganic nutrient bulk will be higher than that proposed by Redfield (1934) (106:16:1), which was calculated from the oceanic average population of phytoplankton.

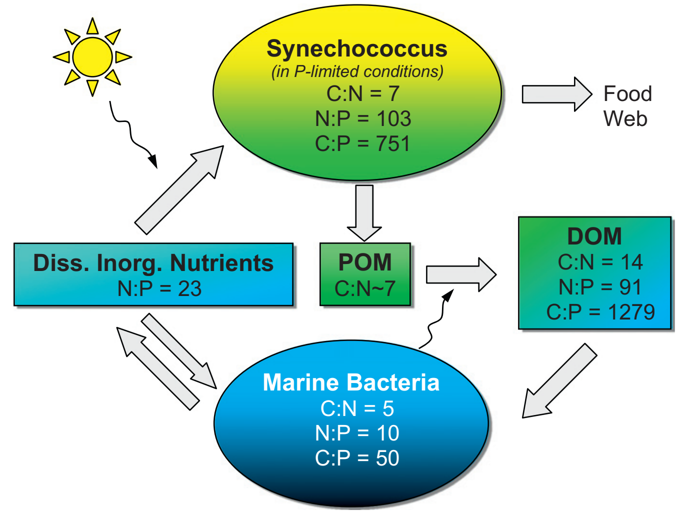

Fig. 7. Schematic representation of the C:N:P ratio in the different compartments. The DOC:DON:DOP ratios were calculated as the average of the ratios in all the samples collected in both cruises. The N:P ratio in the inorganic nutrient pool was calculated from the relationship between DIN and SRP (Fig. 5a). The values for Synechococcus are the average of values reported for Synechococcus WH8012 and WH8103 (Bertilsson et al., 2003). The C:N:P in bacteria were reported in Bertilsson et al., 2003. The POC:PON ratio was observed in POM collected in the sediment trap located at 168 m at station AM1 (Turchetto et al., in press).

The C:N:P ratio in the different compartments (Fig. 7) supports the central role of microorganisms. From the data collected between September 2007 and January 2008 in the sediment trap located at 168 m at station AM1 (Fig. 1), the particulate organic matter (POM) was characterized by a POC:PON ratio of ~7 (Turchetto et al., in press). This ratio is perfectly in agreement with the C:N elemental ratio of 7 for Synechoccocus in P-limited conditions (Bertilsson et al., 2003), suggesting that most of the POM may be constituted by phytoplankton. Unfortunately PON and POP data are not available. Assuming that all DOM is produced in situ, POM mineralization raises C with respect to N in DOM, increasing the C:N ratio (DOC:DON=14), while the N:P ratio (DON:DOP=91) is similar to that reported for Synechococcus (N:P=103). Taking into consideration the C:N:P elemental ratio in marine bacteria (50:10:1) (Bertilsson et al., 2003), DOM used by bacteria has lower N and P (DOC:DON:DOP=1279:14:1) than they require (Fig. 7). As a consequence, they also need inorganic N and P (Kirchman, 2000). Comparison of the N:P ratios in DOM and bacteria indicates that DOM has about nine-fold lower P than N. In order to balance their needs, bacteria will consume about nine-fold more inorganic P than N, further increasing the N:P ratio in seawater. This is just a simplified view of the marine ecosystem functioning, focused on the role of DOM and microorganisms in determining the N and P fluxes between the different compartments. Therefore an important component of the biological pump in the Southern Adriatic (and probably in other areas of the Mediterranean Sea) is Synechococcus (Richardson and Jackson, 2007); this diverges from the classical Redfieldian one, which assumes a vertical transfer of N and P in a ratio of 16. This non-Redfieldian pump only helps to explain the mechanism responsible for the high N:P ratio transfer from surface to deep layers; it does not imply anything about the N:P ratios in the sources. Nevertheless, if the sources were characterized by an N:P ratio lower than the classical biological pump (16), this non-Redfieldian pump would suggest an accumulation of P in either dissolved inorganic matter or in organic bulk. Such an accumulation of P has not been observed in our study, so we can reasonably hypothesize that the transfer occurs involving sources characterized by high N:P ratios.

5. Conclusions

This study provides the first information on the DOM pool and stoichiometry in the Southern Adriatic basin. Our data show that DOM accumulated in stratified water increases its C:N and N:P ratios and that the input of DOM from the Northern Adriatic basin, influenced by terrestrial DOM, results in higher C:N:P ratios. In addition it is noteworthy that minima in DOC, DON and DOP were found in the intermediate layer, occupied by LIW and tEMDW. These water masses had the minimum oxygen levels, indicating a high extent of mineralization.

The concentrations of DOC and DON, as well as DOM stoichiometry, indicate a general similarity with the oceanic waters, with the exception of the general depletion of DOP in surface Mediterranean waters. The observations reported here confirm the low concentration of P, also in its organic form, in this marginal Sea. The general depletion of DOC (or elevation of DON and DOP) observed in the intermediate and deep waters of the Southern Adriatic can be explained by the young age of these water masses, where the effects of mineralization are less than in deep oceanic old waters. The physical dynamics of the area, in particular the deep winter convection and the advection of NAdDW, play a crucial role in shaping DOM stoichiometry and in further masking the effect of mineralization.

Our findings support the idea that the Mediterranean Sea can be considered as a useful model in which to study the C, N and P cycles because the main biogeochemical processes occur in this basin on shorter temporal and spatial scales than in the oceans.

We also suggest that an explanation of the high N:P ratio, typical of the Mediterranean Sea, can be found in DOM stoichiometry and microbial activity.

Finally, this study highlights the need for further efforts to collect new data in order to have a complete overview of DOM stoichiometry in the Mediterranean Sea as well as new information on its temporal dynamics. The N:P molar ratio in both picophytoplankton and prokaryotes should also be investigated in the Mediterranean Sea, in order to gain insight into the high N:P ratio characteristics of the Mediterranean Sea.

Acknowledgments

Most of the experimental work, carried out by G. Civitarese and V. Ibello, took place while they were affiliated to CNR-ISMAR, Trieste (Italy). We wish to thank Luciano Nannicini for his support in DOC analysis. Particular thanks are due to the captains and crews of the RV Dallaporta for their assistance and continuous support during the cruises. This research was supported by the VECTOR Project funded by the Italian Ministry of Research and University. We are grateful to the reviewers for their constructive comments.

References

Aminot, A., Kérouel, R., 2004. Dissolved organic carbon, nitrogen and phosphorus in the N–E Atlantic and the N–W Mediterranean with particular reference to non-refractory fractions and degradation. Deep Sea Research I 51 (12), 1975–1999.

Armstrong, F.A.J., Williams, P.M., Strickland, J.D.H., 1966. Photo-oxidation of organic matter in seawater by ultraviolet radiation, analytical and other applications. Nature 211, 481–483.

Arístegui, J., Duarte, C.M., Agustí, S., Doval, M., Álvarez-Salgado, X.A., Hansell, D.A., 2002. Dissolved organic carbon support of respiration in the dark ocean. Science 298, 1967.

Arrigo, K.R., 2005. Marine microorganisms and global nutrient cycles. Nature 437, 349–355. doi:10.1038/nature04158.

Benner, R., 2002. Chemical composition and reactivity. In: Hansell, D.A., Carlson, C.A. (Eds.), Biogeochemistry of Marine Dissolved Organic Matter. Elsevier San Diego, pp. 59–90.

Bertilsson, S., Berglund, O., Karl, D.M., Chisholm, S.W., 2003. Elemental composition of marine Prochlorococcus and Synechococcus: Implications for the ecological stoichiometry of the sea. Limnology and Oceanography 48, 1721–1731.

Bevington, P.R., Robinson, D.K., 1992. Data Reduction and Error Analysis for the Physical Sciences, second edition, McGraw-Hill, pp. 38–52.

Bonnet, S., Grosso, O., Moutin, T., 2011. Planktonic dinitrogen fixation along a longitudinal gradient across the Mediterranean Sea during the stratified period (BOUM cruise). Biogeosciences 8, 2257–2267. doi:10.5194/bg-8-2257-2011.

Bronk, D.A., 2002. Dynamics of DON. In: Hansell, D.A., Carlson, C.A. (Eds.), Biogeochemistry of Marine Dissolved Organic Matter. Elsevier, San Diego, pp. 153–247.

Cardin, V., Bensi, M., Pacciaroni, M., 2011. Variability of water mass properties in the last two decades in the South Adriatic Sea with emphasis on the period 2006–2009. Continental Shelf Research 31 (9), 951–965. doi:10.1016/j.csr.2011.03.002.

Carlson, C.A., Hansell, D.A., Nelson, N.B., Siegel, D.A., Smethie, W.M., Khatiwala, S., Meyers, M.M., Halewood, E., 2010. Dissolved organic carbon export and subsequent remineralization in the mesopelagic and bathypelagic realms of the North Atlantic basin. Deep-Sea Research II 57 (16), 1433–1445. doi:10.1016/j.dsr2.2010.02.013.

Carpenter, J.H., 1965. The accuracy of the Winkler method for the dissolved oxygen analysis. Limnology and Oceanography 10, 135–140.

Cerino, F., Bernardi-Aubry, F., Coppola, J., La Ferla, R., Maimone, G., Socal, G., Totti, C. Spatial and temporal variability of pico-, nano- and microphytoplankton in the offshore waters of the Southern Adriatic Sea (Mediterranean Sea). Continental Shelf Research, doi:10.1016/j.csr.2011.06.006, in press.

Church, M.J., Ducklow, H.W., Karl, D.M., 2002. Multi-year increases in dissolved organic matter inventories at Station ALOHA in the North Pacific Subtropical Gyre. Limnology and Oceanography 47, 1–10.

Civitarese, G., Gačič, M., Vetrano, A., Boldrin, A., Bregant, D., Rabitti, S., Souvermezoglou, E., 1998. Biogeochemical fluxes through the Strait of Otranto (Eastern Mediterranean). Continental Shelf Research 18, 773–789.

Civitarese, G., Gačič, M., 2001. Had the Eastern Mediterranean Transient an impact on the new production in the Southern Adriatic? Geophysical Research Letters 28 (8), 1627–1630.

Civitarese, G., Gačič, M., Cardin, V., Ibello, V., 2005. Winter convection continues in the warming Southern Adriatic. Eos Transactions American Geophysical Union 86 (45). doi:10.1029/2005EO450002.

Civitarese, G., Gačič, M., Lipizer, M., Borzelli, G.L.E., 2010. On the impact of the Bimodal Oscillating System (BIOS) on the biogeochemistry and biology of the Adriatic and Ionian Seas (Eastern Mediterranean). Biogeosciences 7, 3987–3997. doi:10.5194/bg-7-3987-2010.

Doval, M.D., Pérez, F.F., Berdalet, E., 1999. Dissolved and particulate organic carbon and nitrogen in the Northwestern Mediterranean. Deep-Sea Research Part I 46, 511–527.

Doval, M.D., Hansell, D.A., 2000. Organic carbon and apparent oxygen utilization in the western South pacific and central Indian Oceans. Marine Chemistry 68, 249–264.

Falco, P., Griffa, A., Poulain, P.-M., Zambianchi, E., 2000. Transport properties in the Adriatic Sea as deduced from Drifter data. Journal of Physical Oceanography 30, 2055–2071.

Gačič, M., Borzelli, G.L.E., Civitarese, G., Cardin, V., Yari, S., 2010. Can internal processes sustain reversals of the ocean upper circulation? The Ionian Sea example. Geophysical Research Letters 37, L09608. doi:10.1029/2010GL043216. 2010.

Grasshoff, K., Eharhardt, M., Kremlig, K., 1983. Methods of seawater analysis II edition Verlag Chemie, Weinheim 419 pp.

Hansell, D.A., 2002. DOC in the global ocean carbon cycle. In: Hansell, D.A., Carlson, C.A. (Eds.), Biogeochemistry of Marine Dissolved Organic Matter. Elsevier, San Diego, pp. 685–715.

Hansell, D.A., Carlson, C.A., Repeta, D.J., Schiltzer, R., 2009. Dissolved organic matter in the ocean. A controversy stimulates new insights. Oceanography 22 (4), 202–211.

Hayase, K., Shinozuka, N., 1995. Vertical distribution of fluorescent organic matter along with AOU and nutrients in the equatorial central Pacific. Marine Chemistry 48, 283–290.

Hopkinson, C.S., Fry, B., Nolin, A., 1997. Stoichiometry of dissolved organic matter dynamics on the continental shelf of the Northeastern USA. Continental Shelf Research 17, 473–489.

Hopkinson, C.S., Vallino, J.J., 2005. Efficient export of carbon to the deep ocean through dissolved organic matter. Nature 433, 142–145.

Karl, D.M., Björkman, K.M., 2002. Dynamics of DOP. In: Hansell, D.A., Carlson, C.A. (Eds.), Biogeochemistry of Marine Dissolved Organic Matter. Elsevier, San Diego, pp. 249–366.

Kirchman, D.L., 2000. Uptake and regeneration of inorganic nutrients by marine heterotrophic bacteria. In: Kirchman, D.L. (Ed.), Microbial ecology of the oceans. Wiley series in ecological and applied microbiology. Ralph Mitchell, Series Editor, pp. 261–285.

Klausmeier, C.A., Litchman, E., Daufresne, T., Levin, S., 2004. Optimal nitrogen-to-phosphorus stoichiometry of phytoplankton. Nature 429, 171–174.

Krom, M.D., Woodward, E.M.S., Herut, B., Kress, N., Carbo, P., Mantoura, R.F.C., Spyrese, G., Thingstad, T.F., Wassmann, P., Wexels-Riserf, C., Kitidis, V., Law, C.S., Zodiatis, G., 2005. Nutrient cycling in the south east Levantine basin of the eastern Mediterranean: Results from a phosphorus starved system. Deep Sea Research Part II 52 (22–23), 2879–2896.

Krom, M.D., Emeis, K.C., Van Cappellen, P., 2010. Why is the Eastern Mediterranean phosphorus limited? Progress in Oceanography 85, 236–244.
Loh, A.N., Bauer, J.E., 2000. Distribution, partitioning and fluxes of dissolved and particulate organic C, N and P in the eastern North Pacific and Southern Oceans. Deep-Sea Research I 47, 2287–2316.
Loladze, I., Elser, J.J., 2011. The origins of the Redfield nitrogen-to-phosphorus ratio are in a homeostatic protein:rRNA ratio. Ecology Letters 14, 244–250.
Lucea, A., Duarte, M., Agusti, S., Sondergaard, M., 2003. Nutrient (N, P and Si) partitioning in the NW Mediterranean. Journal of Sea Research 49, 157–170.
Manca, B.B., Ibello, V., Pacciaroni, M., Scarazzato, P., Giorgetti, A., 2006. Ventilation of deep waters in the Adriatic and Ionian Seas following changes in thermohaline circulation of the Eastern Mediterranean. Climate Research 31, 239–256.
Millero, F.J., Sohn, M.L., 1992. Chemical oceanography. CRC Press Inc., pp. 323–352.
Moutin, T., Raimbault, P., 2002. Primary production, carbon export and nutrients availability in western and eastern Mediterranean Sea in early summer 1996 (MINOS cruise). Journal of Marine Systems 33–34, 273–288.
Pantoja, S., Repeta, D.J., Sachs, J.P., Sigman, D.M., 2002. Stable isotope constraints on the nitrogen cycle of the Mediterranean water column. Deep-Sea Research I 49, 127–142.
Poulain, P.-M., 2001. Adriatic Sea surface circulation as derived from drifter data between 1990 and 1999. Journal of Marine Systems 29, 3–32.
Pujo-Pay, M., Conan, P., Oriol, L., Cornet-Barthaux, V., Falco, C., Ghiglione, J.-F., Goyet, C., Moutin, T., Prieur, L., 2011. Integrated survey of elemental stoichiometry (C, N, P) from the western to eastern Mediterranean Sea. Biogeosciences 8, 883–899. doi:10.5194/bg-8-883-2011.
Raimbault, P., Pouvesle, W., Diaz, F., Garcia, N., Sempéré, R., 1999. Wet-oxidation and automated colorimetry for simultaneous determination of organic carbon, nitrogen and phosphorus dissolved in seawater. Marine Chemistry 66, 161–169.
Redfield, A.C., 1934. On the proportions of organic derivatives in sea water and their relation to the composition of plankton. In: Daniel, R.J. (Ed.), James Johnstone Memorial Volume. University Press of Liverpool, Liverpool, pp. 177–192.
Ribera d'Alcalà, M., Civitarese, G., Conversano, F., Lavezza, R., 2003. Nutrient ratios and fluxes hint at overlooked processes in the Mediterranean Sea. Journal of Geophysical Research 108 (C9), 8106. doi:10.1029/2002JC001650.
Richardson, T.L., Jackson, G.A., 2007. Small phytoplankton and carbon export from the surface ocean. Science 315, 838–840.
Roether, W., Schlitzer, R., 1991. Eastern Mediterranean deep water renewal on the basis of chlorofluoromethane and tritium data. Dynamics of Atmosphere and Oceans 15, 333–354.
Santinelli, C., Nannicini, L., Seritti, A., 2010. DOC dynamics in the meso and bathypelagic layers of the Mediterranean Sea. Deep Sea research II 57, 1446–1459. doi:10.1016/j.dsr2.2010.02.014.
Seritti, A., Manca, B.B., Santinelli, C., Murru, E., Boldrin, A., Nannicini, L., 2003. Relationships between dissolved organic carbon (DOC) and watermass structures in the Ionian Sea (winter 1999). Journal of Geophysical Research 108 (C9), 8112. doi:10.1029/2002JC001345.
Turchetto, M., Boldrin, A., Langone, L., Miserocchi, S. Physical and biogeochemical processes controlling particle fluxes variability and carbon export in the Southern Adriatic. Continental Shelf Research, doi:10.1016/j.csr.2011.05.005, in press.
Walsh, T.W., 1989. Total dissolved nitrogen in seawater: a new high-temperature combustion method and a comparison with photo-oxidation. Marine Chemistry 26, 295–311.
Weber, T.S., Deutsch, C., 2010. Ocean nutrient ratios governed by plankton biogeography. Nature 467, 550–554. doi:10.1038/nature09403.