

Dissolved organic nitrogen and phosphorus pools and fluxes in the central Atlantic Ocean

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Abstract

The variation in the concentration and the turbulent fluxes of dissolved organic nitrogen and phosphorus (DON and DOP) across the thermocline in the central Atlantic were studied along a quasi-meridional transect from the Canary Islands to Argentina (22°N to 31°S). In general, DON concentrations were high in surface waters and declined toward the thermocline, whereas DOP concentrations were less variable with depth. Vertical, gradient-driven fluxes of DON and DOP generally involved a downward flux, with a median DON:DOP ratio of 28:1. The downward flux of DON was closely correlated with the nitrate supply to the mixed layer and sufficed to remove an amount of nitrogen equivalent to that associated with the upward nitrate influx into the mixed layer (median = 104%). The downward flux of DON exceeded the supply of nitrate off the NW African coast, where *Trichodesmium* sp. was abundant. The downward flux of DOP was also very closely correlated with the phosphate supply to the mixed layer ($r = 0.87$; $P = 0.0007$), but the downward export of phosphorus as DOP accounted for only 9% of the upward phosphate supply to the mixed layer. There was also evidence of a deep upward flux of DON and DOP from below the thermocline, which, combined with the general downward flux in the upper waters, indicates the presence of a strong sink for DON and DOP within the thermocline, tentatively identified to be microplankton respiration. Our results point to a dominant role of downward DOM fluxes as a path for the removal of nutrients, and probably carbon, from the biogenic layer of the ultraoligotrophic central Atlantic.

Recent methodological developments have revealed a major role for dissolved organic matter (DOM) in oceanic biogeochemical processes (e.g., Toggweiler 1989). DOM has been shown to be a dominant fraction of the nutrient pool in the upper oligotrophic ocean (e.g., Duursma 1961; Thomas et al. 1971; Jackson and Williams 1985), where it appears to play a major role in the export of biogenic elements to the deep ocean (Smith et al. 1986; Toggweiler 1989; Copin-Montégut and Avril 1993; Carlson et al. 1994). The rates of production of dissolved organic nitrogen (DON; Bronk et al. 1994) and phosphorus (DOP; Orrett and Karl 1987) appear to be high in the oligotrophic ocean, probably as a result of a suite of processes that includes sloppy feeding and excretion by functional and dying cells (e.g., Goldman et al. 1985; Andersen et al. 1986; Pujó-Pay et al. 1997; Agustí et al. 1998). Yet DOP and DON appear to have different turnover rates (Jackson and Williams 1985; Smith et al. 1986) and, as a result, are weakly coupled compared with the inorganic and particulate organic forms of these nutrients. This weak coupling may result in export rates that diverge from the Redfield stoichiometry, thereby leading to differential relative losses of nitrogen and phosphorus (Smith et al. 1986).

There is therefore a need to incorporate the size of the pools, their stoichiometry, and the estimated fluxes of DON and DOP into models describing biogeochemical cycling and the control of biological production in the oligotrophic ocean. However, the information required is still sparse and suffers from a severe regional imbalance. Data on DON and

DOP pools in the oligotrophic ocean is largely restricted to the Pacific Ocean (e.g., Thomas et al. 1971; Karl et al. 1993; Libby and Wheeler 1997), and we know little about the tropical Atlantic Ocean (e.g., Duursma 1961; Ridal and Moore 1990). Moreover, concurrent estimates of the concentration and export of nitrogen and phosphorus as dissolved organic compounds (DON and DOP, respectively), which are needed to assess their stoichiometry, are very few (e.g., Smith et al. 1986).

Here we report the size of the DON and DOP pools, their stoichiometry, and estimates of their downward fluxes along a meridional transect across the tropical Atlantic Ocean. We then compare these downward fluxes with the upward fluxes of nitrate and phosphate in an attempt to elucidate the importance of turbulent flux of DOM in the export of nutrients from the upper oligotrophic ocean.

Methods

The study was conducted along a transect across the central Atlantic between the Canary Islands and Argentina (Fig. 1) while we were on board the Spanish research vessel, BIO-Hespérides. Between 21 October and 16 November 1995, 19 stations were occupied to examine the changes in the intensity of the vertical nutrient fluxes in the central Atlantic Ocean. At these stations, water samples were collected by means of 12-liter Niskin bottles mounted on a Rosette frame fitted with a CTD (MARK III or MARK V, Sea Bird). The CTD and rosette casts reached down to 1,000 m and collected water samples from a total of 17–18 depths, with a higher density of samples at the thermocline, where changes in nutrient concentrations are greatest.

Chemical methods—Subsamples were drawn from the Niskin bottles into precleaned polyethylene bottles and were immediately analyzed on board. Samples for DON and DOP

Acknowledgments

This is a contribution to the “Latitude” project (grant AMB94-0739), funded by the Spanish Interministerial Commission of Science and Technology (CICYT). We thank S.V. Smith for helpful criticism, Mario Manriquez and Pedro Jornet for assistance with CTD profiling, A. Lucea for help with nutrient analyses, and the commander and crew of the BIO-Hespérides for help during the cruise.

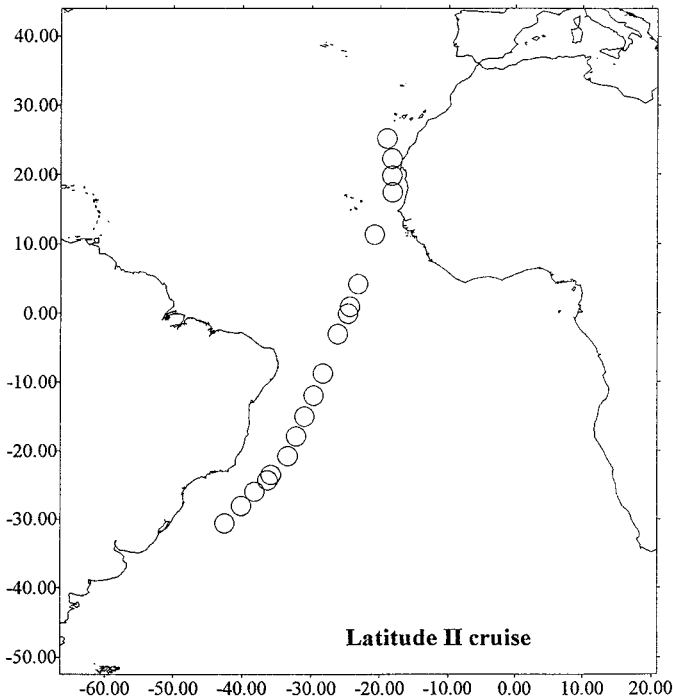


Fig. 1. The position of the stations studied during the "Latitude II" cruise across the Central Atlantic (21 October to 16 November 1995).

determinations were immediately filtered through previously rinsed, 0.2- μm cellulose ester filters mounted on polyvinyl chloride Millex units (Millipore). Controls with distilled water showed that the filtration step yielded no measurable contamination of the samples. Filtered samples were recovered into polycarbonate bottles, which had been cleaned through a process that involved filling them with distilled water and running the oxidation procedure several times, soaking them in diluted hydrogen chloride, and rinsing them with distilled water. Independent samples were analyzed for total dissolved nitrogen (TDN) and total dissolved phosphorus (TDP). TDN and TDP concentrations were determined following oxidation (at 120°C for 30 min) of the filtrate of 20-ml subsamples in alkaline and acidic persulfate, respectively, and through subsequent analysis of dissolved nitrate and phosphate (Grasshoff et al. 1983). Use of ethylenediaminetetraacetic acid standards revealed a nitrogen recovery rate of 97%. The analytical precision, estimated as the standard deviation of replicated samples, was 0.26 and 0.014 μM for TDN and TDP, respectively. DON and DOP were calculated as the difference between total and inorganic nitrogen and phosphorus. Whenever this difference was smaller than 10%, DON and DOP concentrations were considered to be below the resolution of the method, which only occurred for DOP in some deep water samples. As used here, DON includes ammonium, which, however, represents a minor fraction (11%, on average) of this pool. Our choice to include ammonium with the DON pool is the result of the fact that estimates of ammonium concentrations were not available for all samples and that ammonium measurements at such low concentrations are particularly prone to error (Aminot

et al. 1997). The data set on concentrations of DON and DOP is found in an electronic form that is available by anonymous file transfer protocol from atlantis.ceab.csic.es/pub/duarte/dondop.RTF.

Dissolved inorganic nutrients ($\text{NO}_3^- + \text{NO}_2^-$, NH_4^+ , and PO_4^{3-}) were measured spectrophotometrically according to standard methods (Grasshoff et al. 1983). For nitrate plus nitrite in surface samples (upper 30 to 100 m, depending on the thermocline depth) and phosphate, a 10-cm cuvette was used to increase the detection limit in these nutrient-depleted waters. Nitrate plus nitrite concentrations in deep-water samples were determined using a Skalar autoanalyzer. The detection limits of dissolved nutrient concentrations were 0.005, 0.05, and 0.01 μM for spectrophotometric determinations of $\text{NO}_3^- + \text{NO}_2^-$, NH_4^+ , and PO_4^{3-} , respectively, and 0.02 μM for $\text{NO}_3^- + \text{NO}_2^-$ measured with the autoanalyzer.

Flux estimates—Conductivity-temperature-pressure (CTD) data were obtained with a vertical resolution of 10 cm. Salinity and temperature estimates derived from the CTD profiles were calibrated along the cruise using direct salinity measurements from a Guildline Autosal salinometer, calibrated with IAPSO standard seawater (34.993 ‰), and a highly accurate reversible thermometer, respectively. Vertical profiles of salinity and temperature derived from the (corrected) CTD data were screened for errors. We then calculated the density anomaly, σ_t , from temperature and salinity following the algorithms of Fofonoff and Millard (1981), and then averaged the data at 1-m intervals. The vertical gradient in σ_t ($\Delta\rho/\Delta z$) was then used to calculate the Brunt-Väisälä buoyancy frequency (N^2) according to the following equation

$$N^2 = \frac{-g \Delta\rho}{\rho \Delta z} \quad (1)$$

where g is the gravitational acceleration, ρ is the mean density, and Δz is the depth interval.

The horizontal velocity was measured continuously along the cruise using a VM150 narrowband acoustic Doppler current profiler (RD Instruments) mounted on the midhull of the ship. The two horizontal velocity components E-W (u , m s^{-1}) and N-S (v , m s^{-1}) were taken every 1.2 seconds in 8-m bins from the subsurface (16-m) down to the 400-m depth. The calibration of the average velocities was done as recommended by Joyce (1989). The estimates were averaged within 5-min intervals and scanned for errors due to changes in ship position and speed, following King and Cooper (1993) and Saunders and King (1995). Since the estimates of velocity obtained during sampling at the stations were found to contain faulty data, only those obtained during navigation at a uniform speed, estimates that were of much higher quality, were used. Hence, the average vertical structure of velocity at each station was obtained by averaging the velocity profiles obtained in the 15 min preceding and subsequent to the occupation of the stations, while the ship was navigating at cruise speed (about 11–13 knots). The average horizontal velocity profiles obtained for each station were used to calculate vertical shear following the formula

$$\frac{\partial u}{\partial z} = \sqrt{\left[\left(\frac{\Delta u}{\Delta z}\right)^2 + \left(\frac{\Delta v}{\Delta z}\right)^2\right]} \quad (2)$$

The Brunt–Väisälä buoyancy frequency estimates were averaged at intervals corresponding to those used in the calculation of vertical shear, and both estimates were combined to derive an estimate of the vertical turbulent diffusion across the thermocline, following the parametrization developed by Granata et al. (1995), after Gregg (1989)

$$K_p(z) = K_0 \left\langle \frac{S^4}{S_{GM}^4} \right\rangle \quad (3)$$

where $K_p(z)$ is a parametrization of turbulent diffusion at the thermocline, z is depth, K_0 is the background diffusion, which was set to $5 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ (Gregg and Kunze 1991), S_{GM} is the Garrett–Munk shear, which was set to $1.66 \times 10^{-10} [(N^2/N_0^2)]^2$, N_0 was $5.2 \times 10^{-3} \text{ s}^{-1}$ (Gregg 1989), and S was the shear measured over the 8-m bins (broadband).

The thermocline depth was defined as the depth at which maximum stratification occurs (i.e., maximum N^2). This depth was found to correspond to the depth of the biogenic layer (where net primary production > 0) across the transect (Agustí and Duarte 1998). Moreover, the depth of the base of the photic layer was closely correlated ($r = 0.83$) with the depth of the thermocline used as the reference for flux calculations (Agustí and Duarte 1998). This was also true of the depth of the nutricline, for there was also a close correlation between the depth where the nitrate and phosphate gradients were maximal and the depth of the thermocline ($r = 0.656$ and 0.796 , respectively; Duarte et al. unpubl. data). The turbulent flux of dissolved organic nutrients across the thermocline (F_N $\text{mmol m}^{-2} \text{ d}^{-1}$) was, therefore, calculated (assuming gradient transport) as the product between the geometric mean coefficient of vertical turbulent diffusion, $K_p(z)$, $\text{m}^2 \text{ s}^{-1}$, and the gradient in the measured nutrient concentration across the thermocline ($\partial[N]/\partial z$, mmol m^{-4} ; Lewis et al. 1986; Gregg 1989), estimated by linear regression analysis of the observed nutrient concentrations in the individual profiles. F_N was calculated according to the following expression

$$F_N = K_p(z) \frac{\partial[N]}{\partial z} \quad (4)$$

Hence, the calculation of F_N considered the nutrient gradients in a layer of 20 to 60 m, depending on station, centered at the reference level of the thermocline.

A minimum estimate of the turnover rate (T , d^{-1}) of dissolved organic nutrients within a steady-state mixed layer was calculated as follows

$$T = \frac{|F_N|}{M_N} \quad (5)$$

where $|F_N|$ is the absolute vertical turbulent flux of dissolved organic nutrients, and M_N (mmol m^{-2}) is the integrated pool of dissolved organic nutrients within the upper layer (from the surface to the depth where the Brunt–Väisälä buoyancy frequency was maximal)

$$M_N = \int_{z_i}^{z_0} [N] dz \quad (6)$$

The turnover time of dissolved organic nutrients within the mixed layer is, therefore, the inverse of the turnover rate. In fact, the estimates of turnover rate and time obtained represent minimum and maximum values, respectively, for these calculations do not consider other losses of dissolved organic nutrients (e.g., consumption by heterotrophs, photooxidation). Hence, they are partial estimates of the turnover rate and time due to physical processes of vertical mass transfer. The carbon associated to the calculated downward flux of DON was subsequently derived, assuming an average DOC:DON ratio of 12, similar to that observed in other oligotrophic tropical waters (Jackson and Williams 1985; Karl et al. 1993; Williams 1995; Hansell et al. 1997).

Results

The thermocline was deepest (down to 200 m) in the south subtropical gyre and was domed toward the surface between 15°S and 15°N as a consequence of the equatorial divergence and the influence of the Guinea Dome (Mazeika 1968; Voituriez and Dandonneau 1974; Siedler et al. 1992), resulting in a very shallow (30-m) thermocline off the NW African coast (Fig. 2). Here, DON concentrations were high in surface waters and declined along the transect to reach concentrations of $< 5 \mu\text{M}$ in the southernmost water sampled (Fig. 3). DON concentrations in surface waters were somewhat low at the Equator and increased to either side of the Equator (Fig. 3), probably driving a meridional flow of DON. Concentrations of DON were also high in deeper waters around the Equator, and the concentrations in the southernmost waters studied were relatively uniform with depth (Fig. 3). DOP concentrations were highest off the NW African coast (Fig. 3) and were very low ($< 0.1 \mu\text{M}$ DOP) in the southern subtropical gyre and the equatorial waters. There were, however, relatively high DOP concentrations in the thermocline waters north of 10°S (Fig. 3). DON comprised most ($> 90\%$) of the TDN over most of the mixed layer, particularly south of the Equator (Fig. 4). In contrast, DOP only contributed about 30–40% of the TDP in the mixed layer and also constituted a high percentage of the TDP in the southern subtropical gyre (Fig. 4).

DON concentrations were high in surface waters and declined toward the thermocline, although concentrations also tended to increase below the thermocline in about one-half of the stations (Fig. 3). In contrast, the vertical profiles of DOP concentrations were relatively more uniform than those of DON, with low concentrations in surface waters and often a local maximum above the thermocline; DOP concentrations increased with depth for some stations (Fig. 3). Anomalous DON and DOP vertical profiles, involving a disproportionately large increase in concentration with depth, were observed around the northern edge of the southern subtropical gyre. These anomalies were associated with sharp meridional gradients in nitrate and phosphate concentrations (Duarte unpubl. data) as the thermocline sinks toward the gyre area (Fig. 2).

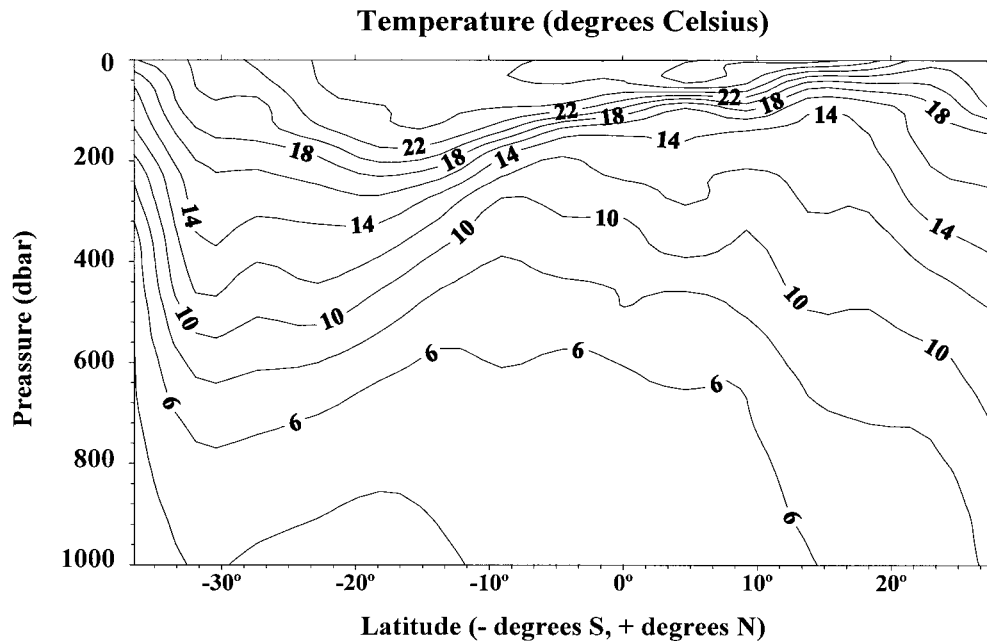


Fig. 2. Contour plot of the vertical variation in temperature along the meridional transect across the Central Atlantic.

DON and DOP concentrations were poorly (albeit significantly; $P < 0.01$) coupled in the upper layer, with this coupling accounting for only 13% of the variance in their concentration. However, there was great variability about the DON:DOP ratio (Fig. 5), with the DOM present in the mixed layer tending to be nitrogen-rich relative to that in the deeper waters (median DON:DOP = 50 and 30, respectively; both exceeded the nitrogen to phosphorus Redfield ratio). The combination of the observed vertical concentration gradients in some of the stations and the estimates of the vertical eddy diffusion coefficient allowed calculation of the vertical, gradient-driven fluxes of DON and DOP (Table 1). DON and DOP downward fluxes were generally higher from the Equator (0.1°S) to the northern end of the transect (19.8°N ; Fig. 6), where the thermocline was established closer to the sea surface. The DON and DOP fluxes were inverted just north of the Equator (0.9°N), where there was an upward flux of DON and DOP from the maximum below the thermocline onto the mixed layer (Fig. 3). The downward fluxes of DON and DOP were, unlike their concentrations, closely coupled ($r = 0.83$; $P < 0.001$), with a median DON:DOP ratio of 28.1 and substantial residual variation (Fig. 7).

The downward flux of DON was closely correlated with the nitrate supply to the mixed layer ($r = 0.71$; $P = 0.0015$; Fig. 8), suggesting a generally close coupling between DON and nitrate fluxes. Indeed, virtually all of the upward nitrate influx into the mixed layer was exported as DON (median = 104%). Moreover, the downward flux of DON exceeded the upward supply of nitrate in some of the stations, particularly those located off the NW African coast (10.3°N ; Fig. 9). This observation suggests the presence of an additional input of nitrogen to the mixed layer, which may be partially supplied laterally through a meridional flux of DON, or, most likely, from atmospheric inputs (Walsh et al. 1992; Cornell

et al. 1995; Libby and Wheeler 1997). Indeed, the station with the highest excess DON flux was characterized by abundant *Trichodesmium* sp. populations ($6,500$ trichomes m^{-3} ; Fig. 9). The downward flux of DOP was also very closely correlated with the upward phosphate supply to the mixed layer ($r = 0.87$; $P = 0.0007$; Fig. 8), although the downward export of phosphorus as DOP accounted for only a median 9% of the upward phosphate supply to the mixed layer. Although these fluxes were very significant, particularly that of DON, they removed only a very minor fraction of the DON and DOP pools present within the mixed layer. The median calculated residence time of dissolved organic nutrients was very long, particularly for DOP, amounting to about 15 yr for DOP and 2.5 yr for DON (Table 1).

Discussion

DON concentrations declined with increasing depth at or near the thermocline, leading to a gradient-driven downward turbulent flux. Moreover, some of the DON and DOP profiles (e.g., that at 11.3°N) showed an increase in DON and DOP concentrations from just below the thermocline to deep waters, suggesting the presence of an upward DON and DOP turbulent flux from below the thermocline. In fact, this subthermocline upward flux often exceeded the downward flux in the upper waters by 5–10-fold. For instance, the deep upward fluxes calculated at the Guinea Dome (11.3°N) and at the southern subtropical gyre (20.8°S) amounted to 199 and 0.94 $\text{mmol nitrogen m}^{-2} \text{d}^{-1}$ of DON and 0.48 and 0.023 $\text{mmol phosphorus m}^{-2} \text{d}^{-1}$ of DOP, respectively, fluxes which were fivefold to 10-fold and >20-fold greater than the downward fluxes of DON and DOP, respectively. The simultaneous subthermocline upward flux and downward

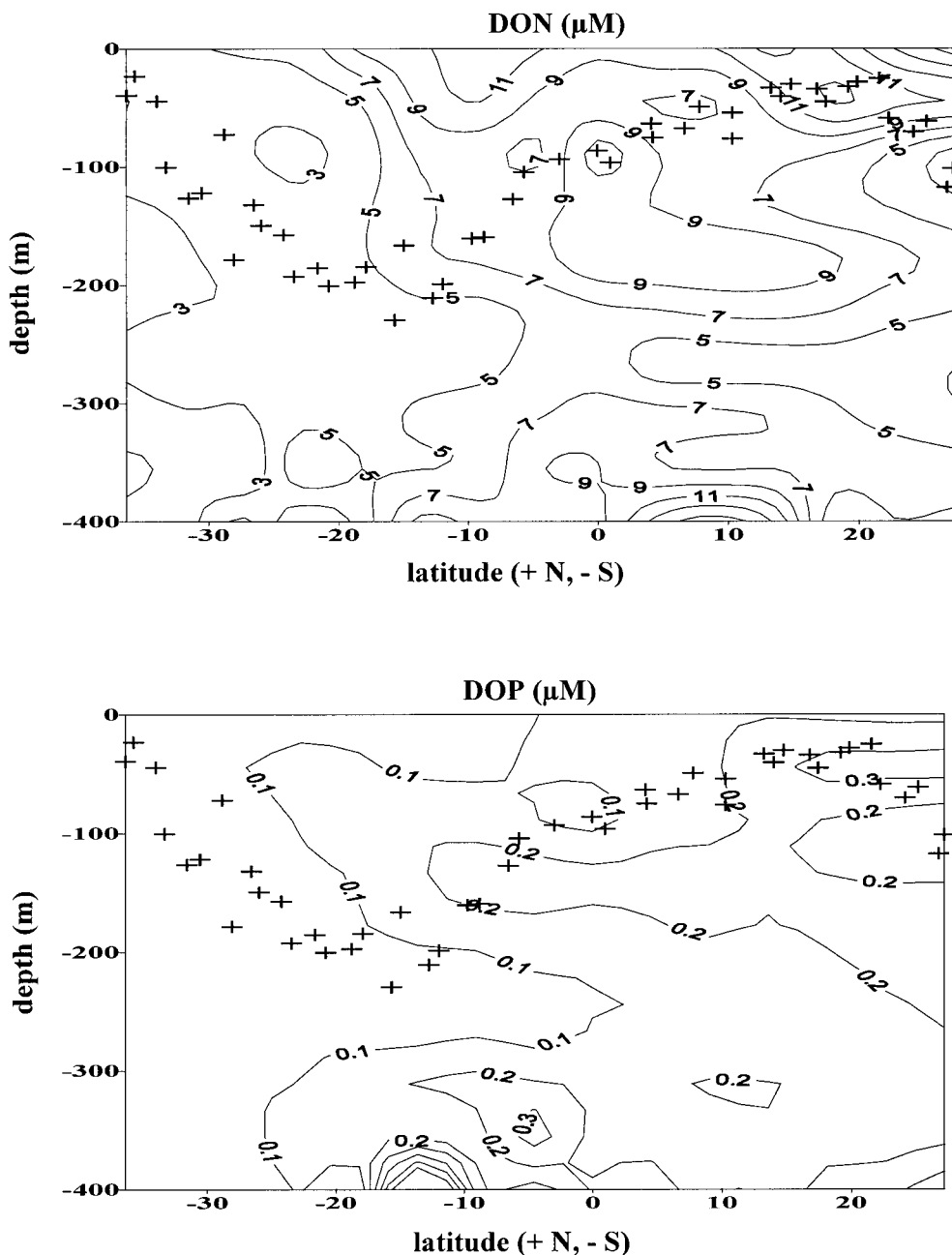


Fig. 3. Contour plots of the vertical variation in DON and DOP along the meridional transect across the Central Atlantic. The crosses indicate the position of the thermocline. The concentrations are in μM .

flux from the mixed layer can only be maintained in the presence of a strong sink for DON and DOP within the thermocline, which we tentatively identify to be microplankton respiration. Microplankton respiration often showed a maximum within the thermocline (Agustí et al. unpubl. data), which could be partially supported from the combined DOM supply from the mixed layer and from the DOM-rich intermediate waters. The average respiration rate ($\pm\text{SE}$) within the thermocline (100 to 150 m) was 2.41 ± 0.37 mmol carbon $\text{m}^{-3} \text{d}^{-1}$ ($N = 17$; Agustí unpubl. data), which, if effective over a 50-m-thick layer, would render a total carbon

consumption of about 120 mmol carbon $\text{m}^{-2} \text{d}^{-1}$. This average respiratory requirement sometimes exceed the overall carbon flux associated with both the upper downward and the subthermocline upward DON flux, which, assuming a $\text{DOC}:\text{DON}$ of 12, was estimated to be 12 mmol carbon $\text{m}^{-2} \text{d}^{-1}$ at the southern subtropical gyre (20.8°S) but which are sometimes lower than the calculated DON-associated carbon supply (e.g., up to $2,800$ mmol carbon $\text{m}^{-2} \text{d}^{-1}$ at the Guinea Dome, 11.3°N). Therefore, the microbial community in the thermocline's interior appears to be a major sink for DOM from both the upper and intermediate waters. The surface

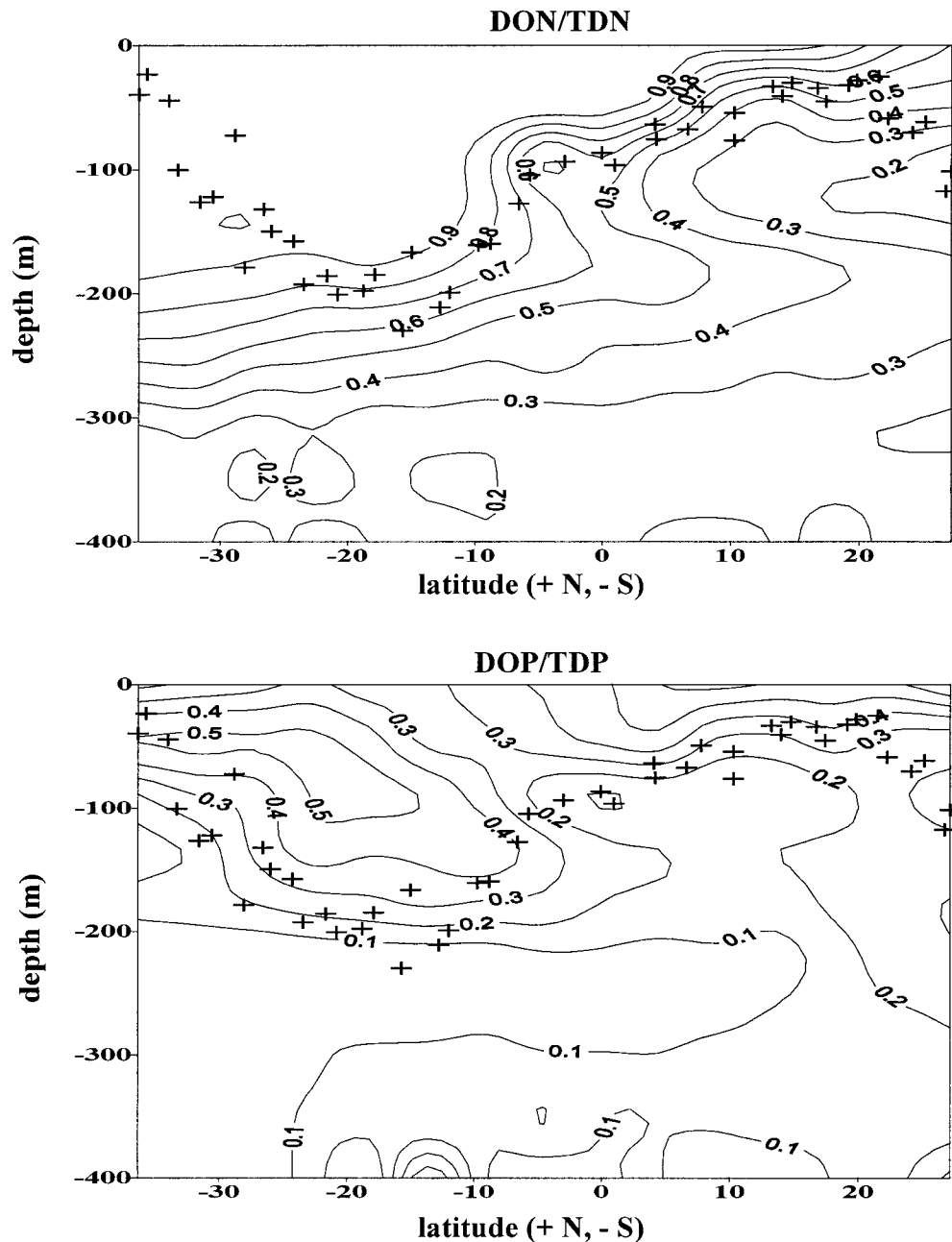


Fig. 4. Contour plots of the vertical variation of the fraction of dissolved nitrogen and phosphorus in organic form along the meridional transect across the Central Atlantic. The crosses indicate the thermocline depth.

pools of DON and DOP, where the highest concentrations were found, are known to be dominated by low-molecular weight compounds, whereas those in deeper waters are more refractory high-molecular weight compounds (Ridal and Moore 1990, 1992; Maita and Yanada 1993). High-molecular weight DOM is known to be relatively depleted in nitrogen and phosphorus and hence is a poor substrate for bacterial growth in the absence of external sources of nitrogen and phosphorus (Amon and Benner 1994). Refractory high-molecular weight compounds are, therefore, exported downward, but the relatively high concentrations of dis-

solved inorganic nitrogen and phosphorus provide the external sources needed for efficient microbial growth and respiration on such substrates within the thermocline.

The downward fluxes of DON and DOP from the mixed layer over the central Atlantic were significant, and they closely correlated with the upward diffusive fluxes of inorganic nutrients. In fact, on average, the downward DON flux accounted for all of the nitrate supplied from the deeper waters to the biogenic layer (median 104%), whereas on median, only 9% of the phosphate supplied from the deeper waters to the mixed layer was exported as DOP. Yet DOP

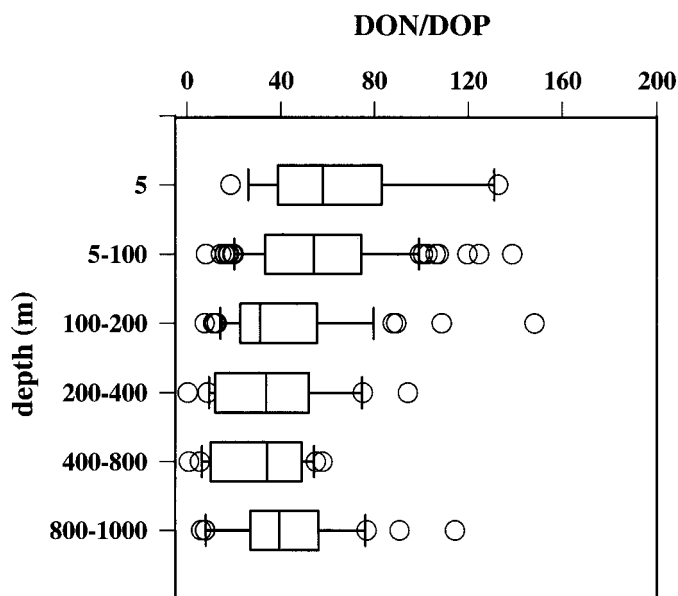


Fig. 5. Box plots showing the vertical variation in the distribution of the ratio of DON to DOP. Boxes encompass 50% of the data, the central line represents the median, the bars encompass the range of 90% of the values, and empty circles represent observations beyond the 90% percentile of the data.

production rates are quite high in the central Atlantic, where they average 7 and $0.002 \mu\text{mol m}^{-3} \text{d}^{-1}$ in the deep-chlorophyll maximum and surface layers, respectively (Cañellas et al. unpubl. data). Hence, the DOP production rate is far greater than our calculated downward flux through the thermocline. These observations imply a much faster recycling of DOP than of DON, which is consistent with available evidence (Pomeroy 1960; Harrison 1983). While DOP remains a large, important phosphorus pool, its comparatively faster recycling allows for a greater retention of DOM-bound

phosphorus within the mixed layer than is associated with DOM-bound nitrogen. These differences in the biogeochemical turnover of DON and DOP in the photic zone have been suggested to be some of the factors that account for the predominance of nitrogen limitation in the ocean (Smith et al. 1986).

Although the downward DON export rates suffice to remove all of the nitrate supplied to the mixed layer from deeper waters, they may represent an even larger (comparatively) loss of carbon. The DOC:DON ratio probably approaches 12 (Karl et al. 1993; Williams 1995; Hansell et al. 1997), whereas the mean ratio of dissolved inorganic carbon to nitrate in the upward turbulent flux approaches the Redfield carbon to nitrogen ratio of 6.6 in the central Atlantic (Duarte unpubl. data). A downward DON flux equivalent to the upward nitrate input would, therefore, transport downward an amount of carbon approximately twice as large as the upward inputs of dissolved inorganic carbon. The sustainability of this process requires a net carbon uptake from the atmosphere equivalent to the upward input of dissolved inorganic carbon (i.e., one-half of the carbon associated with the downward DON flux). Although we did not make any direct measurements, values from Thomas et al. (1995) for an Atlantic equatorial station sampled during the same time of year indicate, when combined with our estimates of the vertical turbulent coefficient at the Equator, a downward DOC flux of about $917 \text{ mmol carbon m}^{-2} \text{d}^{-1}$, which compares well with the value ($884 \text{ mmol carbon m}^{-2} \text{d}^{-1}$) calculated from a downward DON flux of $73.7 \text{ mmol nitrogen m}^{-2} \text{d}^{-1}$ at the Equator (Table 1) and a DOC:DON ratio of 12. Provided a median DON downward flux of $0.12 \text{ mmol nitrogen m}^{-2} \text{d}^{-1}$, which is roughly similar to the median upward nitrate flux in the central Atlantic, and an assumed DOC:DON ratio of 12, the total downward flux of DOM-bound carbon would be $0.52 \text{ mol carbon m}^{-2} \text{yr}^{-1}$. Since the upward dissolved inorganic carbon flux is likely to be only

Table 1. Fluxes, integrated pools within the biogenic layer, and residence time of dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) in the stations sampled. Negative estimates indicate upward fluxes of DON or DOP.

Position		DON			DOP		
Latitude	Longitude	Flux ($\text{mmol m}^{-2} \text{d}^{-1}$)	Pool (mmol m^{-2})	Residence time (yr)	Flux ($\text{mmol m}^{-2} \text{d}^{-1}$)	Pool (mmol m^{-2})	Residence time (yr)
22.3	-18.3	0.0317	300	26	0	15	
19.8	-18.3	4	630	0.4	0.0134	8	1.6
11.3	-20.8	40.5	1,000	0.1	0.017	16	2.6
4.2	-23.2	7.26	612	0.2	0.228	16.5	0.2
0.9	-24.4	-2.54	1,020	1.1	-0.03	14.8	1.4
-0.1	-24.7	73.7	960	0.0	1.67	10.1	0.0
-3.0	-26.2	0.75	980	3.6	0.02	17	2.3
-8.8	-28.3	0.042	1,080	71	-0.0037	21	16
-12.0	-29.7	0.00025	1,751	19000	0.00029	53	500
-15.0	-31.0	0.2189	1,070	13	0.038	53.24	3.8
-17.9	-32.2	0.042	1,080	71	-0.0037	21	16
-20.8	-33.4	0.055	710	35	0.0005	29	160
-23.5	-35.8	0.119	580	13	0.021	27	3.5
-24.3	-36.3	0.0054	590	300	0.0005	13.3	73
-26.0	-38.2	0.069	1,161	46	0.00284	3.27	3.2
-28.1	-40.1	1.42	1,100	2.1	0.0138	11	2.2

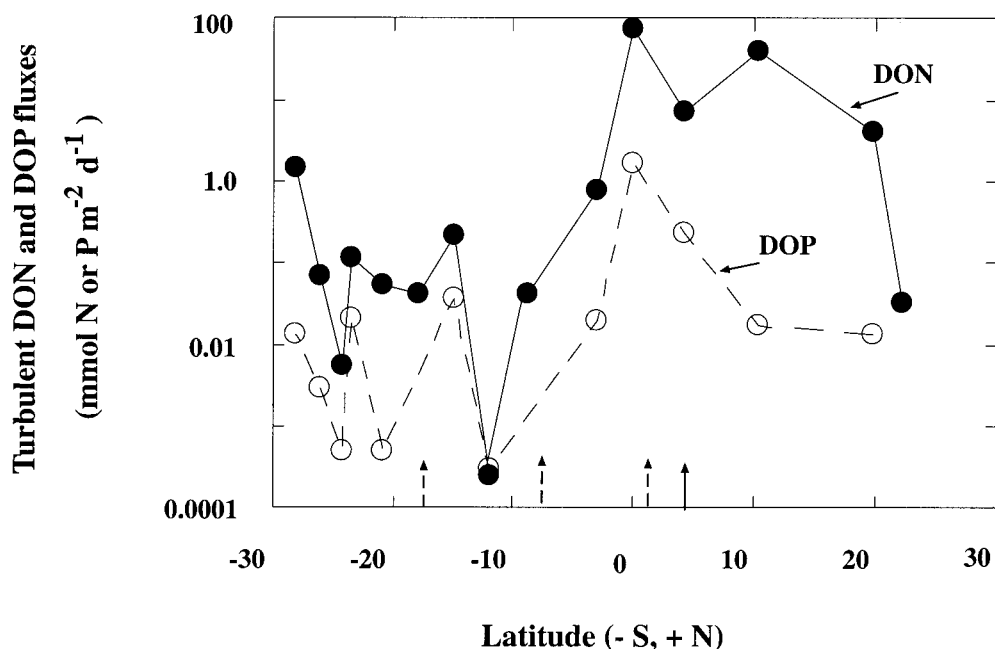


Fig. 6. Latitudinal variation of the DON (filled circles) and DOP (empty circles) turbulent fluxes across the thermocline in the Central Atlantic. Arrows indicate the location of the stations with upward fluxes, broken line arrows indicate upward DOP fluxes, and solid line arrows indicate upward DON fluxes.

one-half of this amount (from a Redfield carbon to nitrogen ratio of 6.6 in the upward turbulent flux of dissolved inorganic carbon and nitrate), then the atmosphere is expected to supply the remaining $0.26 \text{ mol carbon m}^{-2} \text{ yr}^{-1}$; this is well within the range of the available estimates for the tropical Atlantic (from 0 to $1.3 \text{ mol m}^{-2} \text{ yr}^{-1}$; Schlitzer 1989). The calculations above are derived from point measurements and, therefore, may not be representative of the average annual conditions. We believe, however, that they are relevant at a seasonal time scale, because (1) the turnover of DON

and DOP is very long (Table 1), so that rapid fluctuations in concentrations are unlikely, and (2) the thermocline and the current patterns in the study area are also rather stable at the seasonal time scale.

Our finding that the downward export of DON suffices to remove most or all of the nitrate supplied from deep waters to the upper oligotrophic Atlantic Ocean suggests that this oceanic province may be a site of active carbon uptake from the atmosphere, as the observations by Karl et al. (1997) indicate is the case for the tropical Pacific. Tentative calculations of the magnitude of this uptake are consistent with available estimates, suggesting an active role of DOM downward flux in the sequestration of carbon from the atmosphere. Yet the calculated input of carbon from the atmosphere probably comprises both CO_2 and the deposition of organic carbon, which may be significant even in open oceanic areas (e.g., Heikes et al. 1996).

The observation that the downward flux of DON is roughly equal to, and at places exceeds, the upward nitrate supply to the biogenic layer of the central Atlantic suggests that this upward flux cannot be the only source of nitrogen for the ecosystem. Indeed, Gruber and Sarmiento (1997) reported an excess nitrogen concentration in the central Atlantic (north of the Equator, see their fig. 12) that can only be accounted for by significant atmospheric inputs. Gruber and Sarmiento (1997) assigned most of this excess nitrogen to nitrogen fixation by *Trichodesmium*, the dominant N_2 -fixing taxon in oligotrophic marine ecosystems (e.g., Capone et al. 1997), which blooms prominently in the study area during the entire year (Carpenter 1983); they calculate that it provides about 90% of the input of atmospheric nitrogen (about $80 \text{ mmol nitrogen m}^{-2} \text{ yr}^{-1}$; Gruber and Sarmiento 1997) to

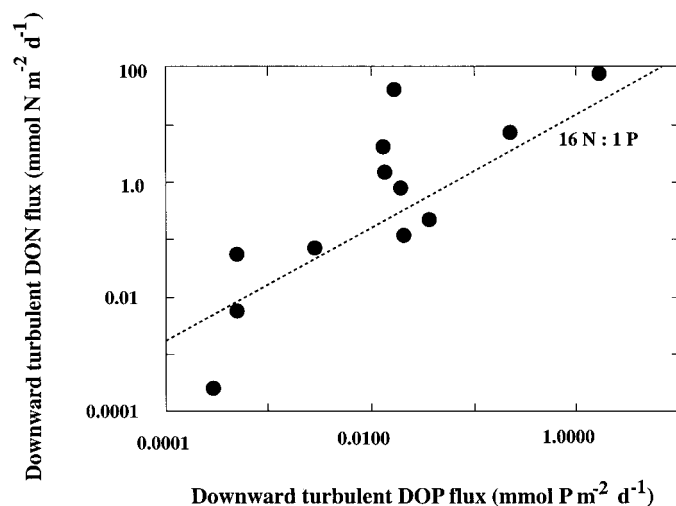


Fig. 7. The relationship between the downward turbulent flux of DON and that of DOP across the thermocline in the Central Atlantic. The dotted line represents the 16:1 line.

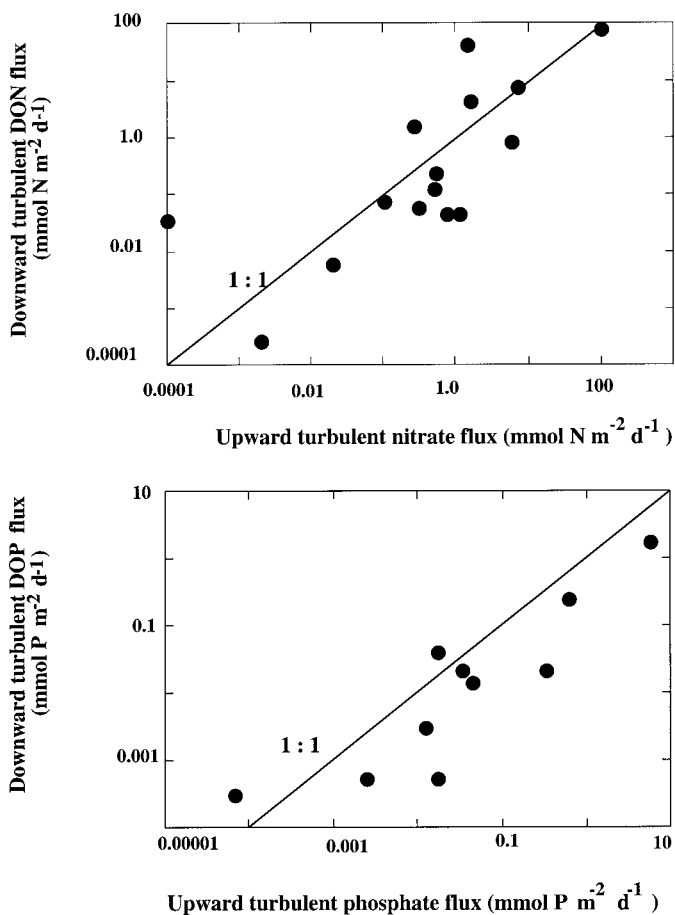


Fig. 8. The relationship between the downward turbulent fluxes of the dissolved organic forms of nitrogen and phosphorus and the upward fluxes of the inorganic nitrate and phosphate across the thermocline in the Central Atlantic. The solid line represents the 1:1 line.

the central Atlantic, the rest of which is the result of atmospheric inputs of DON and dissolved inorganic nitrogen. Indeed, we found that the presence of significant amounts of *Trichodesmium* was associated with an excess downward flux of DON, relative to the upward nitrate input. A significant fraction of the N_2 *Trichodesmium* fixed from the atmosphere is released as DON (Glibert and Bronk 1994), and DON accumulation associated with a *Trichodesmium* bloom has been reported in the subtropical north Pacific Ocean (Karl et al. 1997). Hence, a significant fraction of the nitrogen captured from the atmosphere by nitrogen-fixing plankton may also be exported down as DON, helping account for the overall excess downward nitrogen flux.

The significance of downward fluxes of DON and DOP across the central Atlantic thermocline (from 22°N to 28°S) and of their magnitude relative to the supply of inorganic nutrients from below the thermocline both point to DOM accumulation and fluxes as relevant paths for the export of nutrients in the central Atlantic. Because a dominant fraction of the carbon bound to DOM remains associated with this pool for a long time, the fluxes of biogenic elements as DOM are of considerable significance for biogeochemical cycles.

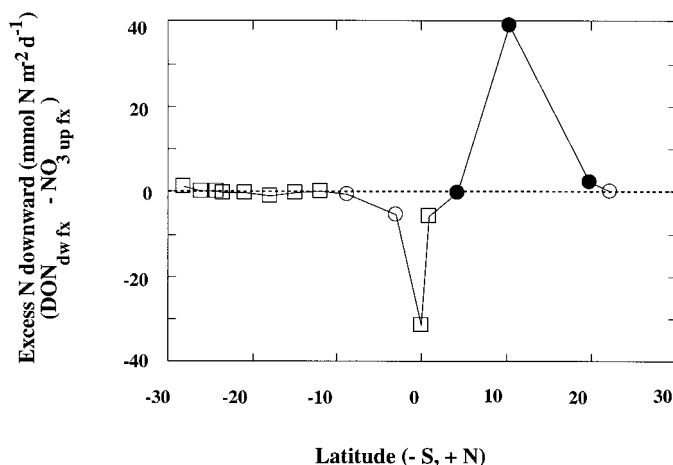


Fig. 9. Latitudinal variation of the excess of the downward flux of DON over the upward flux of nitrate across the thermocline in the Central Atlantic. Empty and filled circles indicate the location of the stations with low and abundant *Trichodesmium* populations, respectively.

Hence, downward DON fluxes, which are made possible by the additional DON produced by nitrogen-fixing organisms or atmospheric DON inputs, are also important paths for the removal of carbon from the biogenic layer of the ultraoligotrophic central Atlantic.

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Received: 10 February 1998

Accepted: 28 August 1998

Amended: 19 October 1998