

Differences in the biological carbon pump at three subtropical ocean sites

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[1] We report primary production of organic matter and organic carbon removal from three subtropical open ocean time-series stations, two located in the Atlantic and one in the Pacific, to quantify the biological components of the oceanic carbon pump. We find that within subtropical gyres, export production varies considerably despite similar phytoplankton biomass and productivity. We provide evidence that the removal of organic carbon is linked to differences in nutrient input into the mixed layer, both from eddy induced mixing and dinitrogen fixation. These findings contribute to our knowledge of the spatial heterogeneity of the subtropical oceans, which make up more than 50% of all ocean area and are thought to spread in the course of CO₂-induced global warming.

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1. Introduction

[2] Due to their global dominance and unexpectedly high export of biogenic carbon, the subtropical gyres of the world ocean are now recognized as critical regions for understanding the role of the ocean in the regulation of atmospheric CO₂ [Emerson *et al.*, 1997 and 2001]. In addition to the physical exchange of CO₂ at the sea surface coupled to ocean circulation processes (solubility carbon pump), the photosynthetic fixation of CO₂ by phytoplankton and subsequent gravitational transport of living and former living particulate matter to the ocean's interior (biological carbon pump) plays an important role in regulating global CO₂ on longer time-scales [Falkowski, 1997] because of its susceptibility to climatic change [e.g., Karl *et al.*, 2001a]. The importance of the subtropics in the biologically mediated carbon export has recently emerged despite their relatively low primary productivity [Emerson *et al.*, 2001]. Not surprisingly, the paradigm shifts about the

role of the subtropics in the biological pump have emerged from the analysis of time-series data, such as the comparative analyses of the US Joint Global Ocean Flux Study (JGOFS) time-series sites near Hawaii (Hawaii Ocean Time-series, HOT; station ALOHA) and Bermuda (Bermuda Atlantic Time-series Study, BATS) [Michaels *et al.*, 2001; Karl *et al.*, 2001b]. Here we compare the carbon and nutrient biogeochemistry of a relatively young time-series site located in the eastern subtropical North Atlantic gyre, the European Station for Time-series in the Ocean, Canary Islands (ESTOC) to its sister station in the western subtropical North Atlantic gyre, BATS, and to the subtropical Pacific time-series station ALOHA. The analysis of the annual cycles of nutrient dynamics, primary and export production indicate that primary production and surface chlorophyll alone are insufficient to constrain the amount of carbon export in the subtropical ocean.

2. Methods

[3] The Hawaii Ocean Time-series station ALOHA (22°45'N, 158°W, 4800 m water depth, <http://hahana.soest.hawaii.edu>) and BATS (31°50'N, 64°10'W, 3200 m water depth, <http://www.bbsr.edu>) sites were initiated in 1988 [Karl *et al.*, 2001b; Steinberg *et al.*, 2001]. The ESTOC (29°10'N, 15°30'W, 3600 m water depth, <http://www.pangaea.de/Projects/ESTOC>, <http://www.iccm.rcanaria.es/>) is located 100 km north of Gran Canaria and Tenerife in the Canary Current, a weak eastern boundary current of the Subtropical North Atlantic gyre. The monthly sampling program at ESTOC was initiated in 1994, and estimates of primary and export production have been obtained since 1996 [Llinás *et al.*, 1999].

[4] *In-situ* ¹⁴C uptake method was applied at HOT and BATS. At ESTOC, ¹⁴C uptake incubations could not be carried out for logistical reasons, instead, a bio-optical model was applied to *in situ* chlorophyll and temperature determined on monthly sampling cruises (assuming 50% cloud cover) [Davenport *et al.*, in press]. When compared to *in situ* application of the ¹⁴C uptake method conducted during one cruise at ESTOC (Oct. 1999), both methods give comparable production rates within 10–20% [Davenport *et al.*, in press].

[5] Shallow particle flux was determined with surface tethered traps in 200 m (ESTOC, BATS) and 150 m depth (HOT). Traps were designed according to Knauer *et al.* [1979] and at ESTOC modified by integrating four cylinders in one larger one to increase sample size. Zooplankton that had entered the traps live were removed on a dissecting scope before sample processing. In addition, AQUATEC time-series traps moored in 500 m water depth were used to

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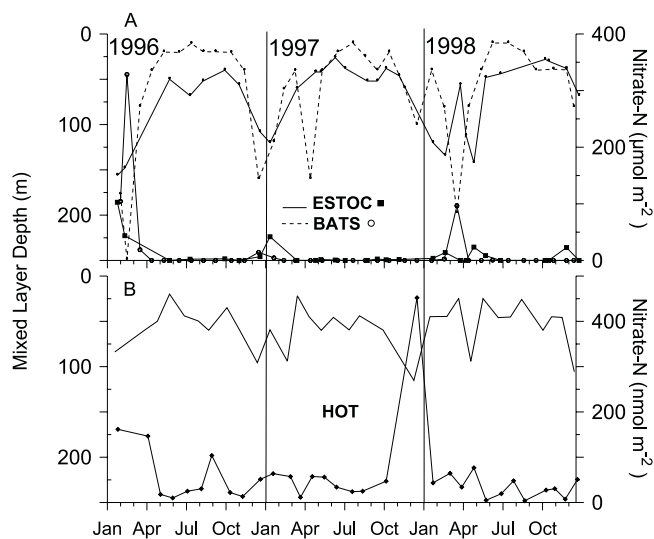


Figure 1. Comparison of mixed layer depth (upper curve; depth at which density σ_θ exceeds surface value by 0.125) and integrated nitrate concentration (lower curve) for ESTOC and BATS (a) and HOT (b). Note the three orders of magnitude change in scales for nitrate concentration between the ESTOC/BATS and HOT data sets.

determine sinking particle flux at ESTOC [Neuer *et al.*, in press]. Trap data were extrapolated to 150 m according to Martin *et al.* [1987].

3. Results and Discussion

[6] Hydrography and concentrations of dissolved nitrate plus nitrite (in the following called ‘nitrate’) differed considerably in the upper water columns of the three time-series stations. Winter mixing at BATS reached much deeper than at either ESTOC (150 m to >250 m compared to 100–150 m, Figure 1a) or HOT (about 100 m, Figure 1b). Measurable (>30 nM) nitrate in the mixed layer was only found during wintertime mixing events at the North Atlantic stations (Figure 1a). Due to the implementation of high sensitivity (1 nM detection) measurement techniques at the subtropical Pacific site, nitrate is measurable year round at station ALOHA but the maxima in winter are two to three orders less than at the other two sites (Figure 1b).

[7] Annually integrated net primary production (PP) was nearly identical at all three sites (Table 2), with slightly lower mean values at ESTOC (Table 1). The major difference is in the C-export (E_{POC} , Figure 2a, Table 1). At HOT and BATS, yearly integrated C-export was approximately

1 mol C m⁻² yr⁻¹ (Table 2). By comparison, at ESTOC C-export was only about 20% of this value, whether determined by surface-tethered traps at 200 m or sediment traps moored to the seabed at a reference depth of 500 m (Tables 1 and 2). This results in a very similar annually averaged export ratio ($ER = E_{\text{POC}}/PP$) at the Sargasso Sea and the subtropical Pacific sites (0.07–0.08), but in a much lower ratio (0.02) for the Canary Island station (Table 2). This discrepancy is also substantiated when comparing the seasonal variability of export ratios (Figure 2b).

[8] When averaged over appropriate spatial and temporal scales, new production (primary production that is based on nitrogen supplied from outside the mixed layer) [Dugdale and Goering, 1967] is equal to export production [Eppley and Peterson, 1979]. Thus one expects that under steady-state conditions, the ratio of new to total production (f -ratio) would be equivalent to ER [Berger and Wefer, 1990]. The classical empirical models based on shallow trap samples that cast the f -ratio or ER as an increasing, non-linear function of PP [e.g., Martin *et al.*, 1987; Pace *et al.*, 1987] produce ratios between 0.15 and 0.20 at 125 m for the range of PP measured for the time-series stations and do not reflect the observed differences; neither do models relating f -ratio to available nitrate [Platt and Harrison, 1985] (see also calculations below) or temperature [Laws *et al.*, 2000] (according to this model, because of colder surface water temperatures at ESTOC compared to BATS or HOT, ER should be higher at ESTOC and in the range of 0.2–0.3). Thus other factors have to be considered that determine the biological carbon export of the subtropical gyres and that are not included in these models.

[9] Lower export production at ESTOC when interpreted in a new production context, is indicative of a lower supply of new nutrients into the productive euphotic zone. One supply mechanism is provided by the deepening of the mixed layer in winter (see Figure 1). An estimation of new production based upon the draw down of each measurable nitrate pulse in the mixed layer (Figure 1) for the three stations and three years results in comparable estimates for BATS and ESTOC (0.01–0.5 mmol N m⁻² yr⁻¹ and 0.06–0.2 mmol N m⁻² yr⁻¹, respectively) but values lower by three orders of magnitude for HOT (0.3–0.6 μmol N m⁻² yr⁻¹). The nitrate concentration in the mixed layer is a result of both nitrate input and uptake; therefore these new production estimates are conservative. But the comparison does not explain the lower export ratios found for ESTOC, nor is it consistent with the similarity of export ratios found for HOT and BATS. Alternatively, mesoscale eddies, usually not adequately resolved by most standard sampling programs, have been shown to supply a significant portion of new nutrients in the Sargasso Sea, considerably more

Table 1. Mean, Standard Deviation (SD) of the Mean, Range and Number of Measurements (n) of Daily Integrated Primary Productivity (PP, 0–150 m) and Export Flux (E_{POC} , 150 m) From the Three-Year Data Set of Time-Series Stations BATS, HOT (¹⁴C-method; surface tethered traps) and ESTOC (bio-optical model; shallow moored/surface-tethered traps)

	PP mg C m ⁻² d ⁻¹			E_{POC} mg C m ⁻² d ⁻¹		
	BATS	HOT	ESTOC	BATS	HOT	ESTOC
Mean ± SD	536 ± 139	472 ± 137	408 ± 93	29.2 ± 13.8	28.9 ± 9.6	7.2 ± 4.6/5.1 ± 2.7
Range	286–836	170–680	244–713	13–86	11–56	1–19/2–11
n	32	29	35	32	29	55/14

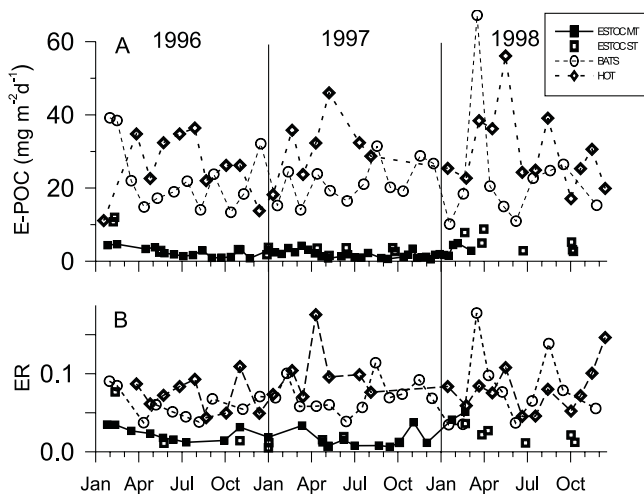


Figure 2. (a). Seasonality of particulate organic carbon flux (E_{POC}) determined at the three time-series stations with surface tethered traps (ST) in 200 m (BATS and ESTOC) and 150 m depth (HOT) for the three-year period 1996–1998. For ESTOC, flux is also shown for moored trap at 500 m depth (MT). B. Seasonality of export ratios at the three stations (see also Table 2).

than wintertime convection [McGillicuddy *et al.*, 1999]. Oschlies and Garçon [1998] show that there are clear differences in eddy-induced nitrate input between western and eastern subtropical Atlantic with rates ranging from $0.2\text{--}0.5 \text{ mol N m}^{-2} \text{ yr}^{-1}$ for the Sargasso Sea and $0.01\text{--}0.1 \text{ mol N m}^{-2} \text{ yr}^{-1}$ for the Canary Islands location. The Atlantic Ocean model estimates for nitrate flux into the mixed layer are much higher than the nitrate input due to wintertime convection by about three orders of magnitude and emphasize the importance of this nutrient supply mechanism for the subtropical oceans. We hypothesize that this difference in associated nutrient input between the Sargasso Sea and the Canary Island sites is large enough to contribute to the observed differences in export ratio. Quantification of mesoscale eddy activity has not been conducted for the Pacific station, but recent field observations suggest that it may be an important nutrient source [Letelier *et al.*, 2000].

[10] Another significant source of new nitrogen in the subtropical gyres of the world oceans is dinitrogen fixation. At both HOT and BATS, nitrogen fixation has emerged as an important process supplying 30% or more of new nitrogen to the mixed layer [Gruber and Sarmiento, 1997], both based

on biology and nutrient dynamics, [Karl *et al.*, 2001c] and molar ratios of dissolved inorganic nitrogen and phosphorus higher than the classical Redfield ratio [Redfield *et al.*, 1963] of 16N:1P [Michaels *et al.*, 1996; Wu *et al.*, 2000]. Nitrogen fixation has not been measured directly at ESTOC, but we compared nutrient ratios of all three time-series stations (Figure 3) to determine if there was evidence for nitrogen fixation at the Canary Islands station. In contrast to BATS and HOT, the nitrate:phosphate ratio conformed to the expected Redfield ratio at ESTOC, providing an indication that nitrogen fixation is not an important process for supplying new nitrogen at the Canary Island station. Note that for the Pacific site, Karl *et al.* [2001c] show a discrepancy between the nutrient ratios of the inorganic and the much larger dissolved organic nutrient pools; the N:P ratios of the latter are above Redfield ratio, indicating an imbalance between the nutrient pool available for primary production and the photosynthetically-derived dissolved organic matter.

[11] Further evidence for the lack or low rates of nitrogen fixation at ESTOC is obtained by the analysis of stable nitrogen isotope ratios ($\delta^{15}\text{N}$) in the suspended and sinking particulate pools. The particulate and dissolved nitrogen pools stemming from nitrogen fixation has a low abundance of ^{15}N (the $\delta^{15}\text{N}$ of atmospheric N_2 is 0); this has been shown for HOT (value of 1.53‰ for particulate matter following summer export pulse) [Karl *et al.*, 1997] and BATS (suspended particles $-0.2 \pm 0.6\text{‰}$; 0–100 m) [Altabet, 1989]. In contrast, higher $\delta^{15}\text{N}$ values were measured at ESTOC of 5.1‰ (suspended particles, 0–200 m, Sept 1998), $4.6\text{‰} \pm 0.7\text{‰}$ (sinking particles collected with surface tethered traps, 200 m, Feb. 1998–May 1999, $n = 7$), and 4.2‰ (sinking particles collected with moored traps, 500 m, Nov 1995–Sept 1997; Freudenthal *et al.*, 2001), close to the isotopic value of average seawater nitrate of 5‰ . Thus nitrogen isotope values and N:P ratio both indicate that nitrogen fixation cannot be a dominant source of new nitrogen for primary production at ESTOC. We hypothesize that this lack at ESTOC of an otherwise notable source of new nutrients is in part responsible for the low export ratios.

4. Conclusions

[12] The lower input of new nitrogen both by smaller mesoscale eddy activity and lack of significant nitrogen fixation at ESTOC may be characteristic of the eastern basin of the subtropical North Atlantic as a whole, thus pointing to a dichotomy of biological carbon pump efficiency in the subtropical Atlantic. The comparison of the seemingly similar subtropical ocean sites shows that a lower input of

Table 2. Yearly Integrated PP, E_{POC} and ER (E_{POC}/PP) for the Three Time-Series Stations

	PP mol C m ⁻² yr ⁻¹			E_{POC} mol C m ⁻² yr ⁻¹			ER		
	BATS	HOT	ESTOC	BATS	HOT	ESTOC ^a	BATS	HOT	ESTOC ^b
1996	16.3	15.1	11.9	1.4	0.8	0.24/ 0.16	0.086	0.05	0.017
1997	13.3	13.3	12.0	1.3	1.2	0.16/ 0.16	0.098	0.092	0.013
1998	13.9	15.3	11.7	0.7	0.9	-0.20	0.050	0.06	0.017
AVG	14.5	14.6	11.9	1.1	1.0	0.2	0.078	0.068	0.016

^a Shallow moored/surface tethered trap. Surface tethered trap value of 1996 and 1997 composite of both years.

^b Mean of moored and surface tethered traps.

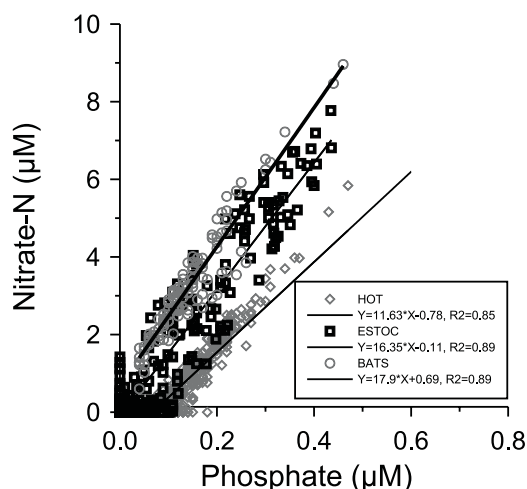


Figure 3. Plot and linear regression of dissolved inorganic phosphate versus nitrate measured for the three time series stations for 1996–1998, 0–500 m for BATS and 0–200 m for HOT and ESTOC. Classical Redfield molar ratio of N:P is 16:1 which is only approximated by nutrient ratios found at ESTOC.

new nutrients does not result in lower primary production per se but rather influences the removal efficiency (export ratio) of biologically produced carbon into the ocean's interior. This study exemplifies the potential of long-term open ocean time-series stations as test beds for hypotheses and paradigms that shape our knowledge of the role of the ocean biota in global climate change.

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