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# Primary Productivity and the Flux of Dissolved Organic Matter in Several Marine Environments

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## Abstract

Primary productivity and the flux of $DO^{14}C$, dissolved saccharides (DSAC) and dissolved free primary amines (DFPA) were followed in the Sargasso Sea, Caribbean and upwelling waters of Peru. Average carbon fixation rates were 42.8, 292.8 and 4791.6 mg C $m^{-2}$ $d^{-1}$, respectively, with nocturnal respiration rates ranging from 9.8–16.3% of gross photosynthesis for the 3 areas. The release of $DO^{14}C$, as a percentage of the total carbon fixed in photosynthesis, was non-detectable in the Sargasso Sea, and 3.2 and 4.4% for the Caribbean and Peruvian phytoplankton communities. Few significant changes in DSAC concentrations were recorded over a 36-h incubation period in the Sargasso Sea and Caribbean stations, whereas light-dependent accumulations of DSAC and DFPA were noted in Peruvian stations which were strongly correlated with total phytoplankton productivity. In the Peruvian stations, the average accumulation rate was 234 mg DSAC-C $m^{-2}h^{-1}$ while the average rate of nocturnal decomposition was 141 mg DSAC-C $m^{-2}h^{-1}$; diurnal and nocturnal rates of DFPA accumulation and decomposition were similar (2 mg DFPA-C $m^{-2}h^{-1}$). These data were used to calculate bacterial production in the upwelling waters of Peru. A general discussion of $^{14}C$-techniques and routine analytical techniques for DSAC analysis is presented, as DSAC flux exceeded $DO^{14}C$ flux by 17-fold in coastal Peruvian stations.

## Introduction

The flux of dissolved organic matter (DOM) in the marine environment is generally associated with lower trophic levels, with reduced carbon compounds produced by phytoplankton and utilized and mineralized by the bacterioplankton. Zooplankton and protists may also act as agents in the production of soluble organic matter via "sloppy feeding", resulting in elevated DOM concentrations at zooplankton maxima (Lampert, 1978; Burney *et al.*, 1979).

Most recent data on the release of organic matter indicates $DO^{14}C$ released by healthy growing marine phytoplankton is a relatively constant fraction of the $^{14}C$ incorporated into cells (Mague *et al.*, 1980) and that little $^{14}C$ incorporated during active photosynthesis is released as $DO^{14}C$, with percentage extracellular release (PER) < 10% of total carbon fixation (Williams and Yentsch, 1976; Sharp, 1977; Mague *et al.*, 1980). However, $^{14}C/^{12}C$ disequilibrium within the various intracellular organic pools in phytoplankton may result in serious underestimates of total organic carbon release (Saunders, 1972) if total release is based solely on accumulation rates of $DO^{14}C$.

Carbohydrates and amino acids comprise significant portions of the organic matter released by phytoplankton (Hellebust, 1965). The production of extracellular carbohydrates in laboratory phytoplankton cultures has been observed by many investigators (Guillard and Wangersky, 1958; Hellebust, 1965, 1974), particularly in diatom cultures (Lewin, 1955; Lewin *et al.*, 1958; Handa, 1970; Allan *et al.*, 1972; Myklestad and Haug, 1972; Myklestad *et al.*, 1972; Myklestad, 1974; Smestad *et al.*, 1974; Haug and Myklestad, 1976; Percival *et al.*, 1980) with increasing extracellular accumulations noted under N or P limitation and/or senescence. Nutrient concentrations are low in oceanic areas, which may explain slower algal growth rates *in situ* than in optimal laboratory conditions. In that case, saccharide release might form a large pool of reduced carbon in the marine environment.

Since $^{14}C$ incorporation is a light-dependent process and $DO^{14}C$ release may be approximately proportional to $^{14}C$ incorporation, the concentration of DOM should peak during daylight hours and subsequently decline during the nocturnal period due to a cessation of photosynthetic $^{14}C$ fixation and heterotrophic uptake of the released material. The present study was conducted to ascertain the relation-

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ship between primary productivity and the release of $DO^{14}C$, dissolved saccharides (DSAC) and dissolved free primary amines (DFPA) in oligotrophic and eutrophic oceanic areas. Heterotrophic activity of the bacterioplankton was estimated from the nocturnal changes in DOM, enabling estimation of bacterial productivity for the marine areas. Monitoring changes in activity of the $^{14}C$-labeled phytoplankton over 24 h would also identify turnover for cellular carbon in photosynthesis and respiratory metabolism.

## Materials and Methods

In October–December, 1977, as part of the ICANE (Investigation Cooperativa de la Anchoveta y su Ecosistema-Canada, Peru), the C.S.S. "Baffin" was engaged in an oceanographic cruise from Nova Scotia, Canada to Peru (Fig. 1). For the present study, daily hydrocasts were made at 19 stations: in the Sargasso Sea, Stations 006, 008, 010; in the Caribbean, Stations 012, 013, 014, 021; and off the coast of Peru, Stations 193, 197, 204, 213, 222, 242, 251, 278, 314, 321, 324 and 336. Samples were collected from depths to which 100, 50, 25, 11 and 1% of incident light penetrated as determined from the secchi disc depth. Surface samples of red tide blooms were obtained from bucket grabs at Stations 194 and 204 A. These are discussed separately in the text.

Primary productivity (particulate and dissolved organic carbon formation) was determined using modified $^{14}C$-techniques. One-liter samples from each depth were supplemented with 20 $\mu$Ci $Na_2{}^{14}CO_3$ (0.3 mCi $\mu M^{-1}$), and incubated in simulated *in situ* deck water baths for a period of 48 h. Subsamples were removed at intervals for estimates of productivity and DOM concentrations. The long incubation period was employed to obtain estimates of primary productivity over 2 d for calculation of division rates. One-liter bottles were used in the incubations to reduce wall effects expected in bottles of smaller volume (300 ml).

For primary productivity estimates, a 20–100 ml subsample was removed initially and at sundown and sunrise over 2 complete diel cycles. Cells were filtered onto 0.45 $\mu$m Millipore® filters under low vacuum, fumed over concentrated HCl for $\geqq$ 30 s and placed in 15 ml Aquasol® I or II (New England Nuclear). The filtrate was acidified (pH = 2.1) and bubbled with air (1 h) and a 5-ml aliquot was pipetted into 15 ml of cocktail. Activities of filters (particulate-$^{14}C$) and aqueous ($DO^{14}C$) samples were determined with liquid scintillation. Carbon incorporation was

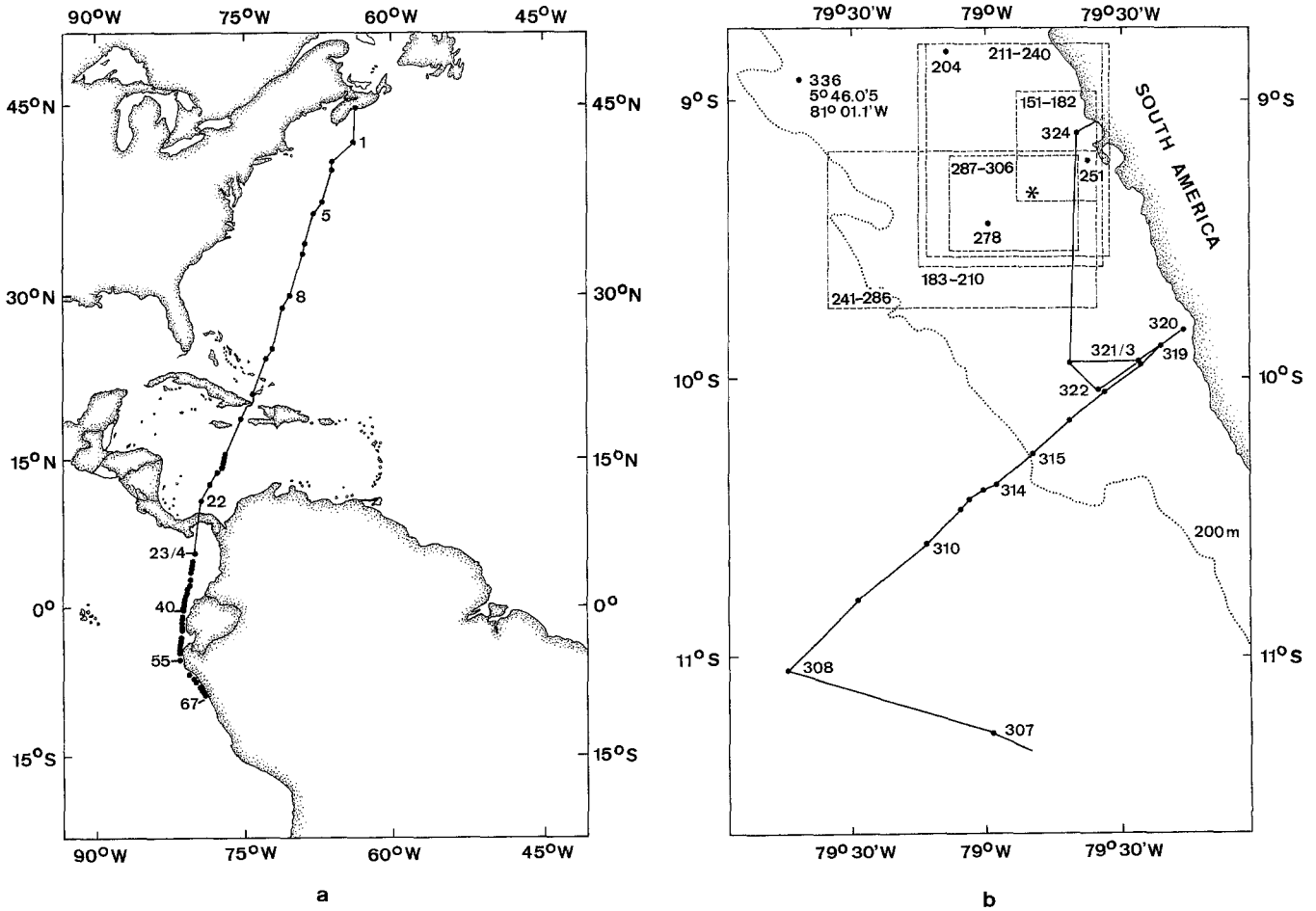


**Fig. 1.** Project ICANE cruise track aboard C. S. S. "Baffin", October–December, 1977 (adapted from Doe, 1978). (**a**) Sargasso Sea and Caribbean stations; (**b**) Peruvian shelf stations; * indicates Stations 193, 194, 197, 213, 222 and 242

calculated according to Vollenweider (1974). Carbon fixation rates were expressed $h^{-1}$ and water column rates $m^{-2}$ determined by trapezoidal integration. The percentage extracellular release (PER) was calculated as the ratio of $DO^{14}C$ in the filtrate to total productivity [($DO^{14}C$/particulate-$^{14}C + DO^{14}C$) × 100]. The ratio of respiratory metabolism to gross photosynthesis (R/R + P) (expressed as a percent) was estimated as [NP/(DP + NP)] × 100, where NP = nocturnal particulate carbon fixation $[12\ h]^{-1}$ and DP = diurnal particulate carbon fixation $[12\ h]^{-1}$. Division rate (K) was calculated as $0.5\ (3.32/\Delta t) \log C_2/C_1$, where $C_1$ and $C_2$ were C-fixation rates at 12 and 36 h.

Significant differences ($P \leqq 0.1$) in activity (cpm) between diurnal and nocturnal particulate samples were determined by computing the t statistic from $cpm_2 - cpm_1 / (\sigma_1^2 + \sigma_2^2)^{1/2}$, where $cpm_1$ and $cpm_2$ represent activity at successive time periods. If $DO^{14}C$ productivities over successive sampling times did not exceed 1.65 $\sigma$, within 90% of a normal distribution, the rates were considered the same.

Initial concentrations of nitrate, nitrite, ammonia, phosphate and silicate at each depth were determined by automatic colorimetric methods (Whitledge *et al.*, 1980). Samples were either analyzed immediately or stored at 4 °C in the dark for ≦ 24 h. All nutrient samples were filtered through pre-combusted Reeve-Angel 984H glass fibre filters. Chlorophyll *a* was determined from fluorescence measurements of 90% acetone-extracted samples.

Dissolved saccharides (DSAC) were determined by the MBTH procedure (Burney and Sieburth, 1977). Five-ml samples were filtered through pre-combusted Reeve-Angel 984H filters, frozen and subsequently analyzed with a Beckman DU Spectrophotometer. Two replicates were taken from each 1-liter sample initially, at dark, dawn and at dark the following day. The mean of the 2 samples was used in all calculations. Results were expressed in glucose-equivalents $l^{-1}$ from glucose standards prepared in 3.5% NaCl solutions. Saccharide carbon was computed from 0.4 times the saccharide concentration.

Dissolved free primary amines (DFPA) were determined using the Fluorescamine technique (modified from North, 1975). Duplicative five-ml subsamples were removed from each 1-liter sample initially and at sundown, sunrise and sundown the following day. Each 5-ml sample was buffered to pH 9.4 with a sodium borate-sodium hydroxide buffer followed by the addition of 2 ml Fluram® stock solution (20 mg Fluorescamine/100 ml anhydrous redistilled acetone) with vigorous shaking. The white precipitate was dissolved by the addition of 0.5 ml 0.1 N HCl. Sample fluorescence was determined on an Aminco SPF-125 fluorometer at excitation and emission wavelengths of 395 and 495 nm, respectively. Glycine standards were prepared in a 3.5% NaCl solution. Blanks consisted of sample fluorescence without the addition of Fluram®. DFPA carbon was calculated assuming average composition was glycine (DFPA × 0.32).

A daily precision limit was calculated for each analysis: $[(\Sigma s_s^2 + s_b^2 \ldots s_n^2)/n]^{1/2}$, where $s^2$ is the variance term for each pair of absorbance or fluorescence readings at each station and n is the number of samples. The daily precision limits for each analysis are presented in Table 1.

**Table 1.** Daily precision limits for DSAC and DFPA analyses. Values are standard deviations from the sum of all replicate variability $d^{-1}$

| Station | DSAC ($\mu g\ l^{-1}$) | DFPA ($\mu g\ l^{-1}$) |
|---|---|---|
| 006 | 81.2 | 0.61 |
| 008 | 65.7 | 0.54 |
| 010 | 74.8 | 0.69 |
| 012 | – | 0.74 |
| 013 | 265.8 | 0.26 |
| 014 | 152.4 | 0.51 |
| 021 | 146.6 | 0.61 |
| 193 | 68.3 | 1.18 |
| 197 | 61.5 | 2.52 |
| 204 | 174.6 | 3.91 |
| 213 | 85.4 | 1.91 |
| 222 | 153.5 | 1.95 |
| 242 | 144.9 | 1.74 |
| 251 | 355.8 | 6.06 |
| 278 | 103.0 | 1.52 |
| 314 | 180.0 | 1.36 |
| 321 | 161.3 | 2.86 |
| 324 | 147.5 | 2.68 |
| 336 | 85.8 | 2.14 |

Significant changes in integrated DSAC and DFPA concentrations between successive sampling periods (initial-sundown, sundown-sunrise) were determined by calculating the paired-t statistic for each station. The mean concentration of the two replicate subsamples was computed for each light depth (100, 50, 25, 11 and 1% $I_0$) in each subsampling period; significant differences ($\alpha = 0.05$) between the means of successive time periods were obtained. Hourly rates were calculated by dividing concentration differences by the incubation time and the depth of the euphotic zone.

## Results

### Phytoplankton Metabolism and Biomass

Primary productivity, respiration rates, chlorophyll *a* concentrations, growth rates and nutrient concentrations increased from the oligotrophic regions of the Sargasso Sea and Caribbean to the upwelling waters of coastal Peru (Table 2). The metabolic rates increased by two orders of magnitude, with average carbon fixation and respiratory rates (uncorrected for $DO^{14}C$ excretion) of 4.1 and 0.5 mg C $m^{-2}\ h^{-1}$, respectively, in the Sargasso Sea and 451.8 and 52.5 mg C $m^{-2}\ h^{-1}$ for the Peruvian euphotic zone. Two other indices of phytoplankton metabolism, growth rates and assimilation ratios, also followed similar trends, increasing from nutrient-poor to nutrient-rich waters. The growth rate increased from 0.11 to 0.55 divisions $d^{-1}$ from the Sargasso Sea to Peru, while the assimilation ratio (mg C mg chl $a^{-1}\ h^{-1}$) rose from 0.4 to 4.0 in the transit.

**Table 2.** Distribution of algal metabolism and biomass and nutrient concentrations for Sargasso Sea, Carribean and Peruvian shelf stations from October-December, 1977. Diurnal particulate productivity (DP), production of dissolved organic $^{14}$carbon (D-DO$^{14}$C) and nocturnal carbon respiration rates (NP) and production of dissolved organic $^{14}$carbon (N-DO$^{14}$C) are presented in mgC m$^{-2}$ h$^{-1}$. The fraction of carbon fixed during photosynthesis and subsequently released as D-DO$^{14}$C is presented as PER (D-DO$^{14}$C/(DP+D-DO$^{14}$C)). Chlorophyll *a* (Chl *a*) is presented in mg m$^{-2}$; the assimilation ratio (AR) is presented as mgC mg chl *a*$^{-1}$ h$^{-1}$. All nutrients are presented as mg-at m$^{-3}$. ND indicates not detectable

| Stn | (DP) Particulate Productivity | D-DO$^{14}$C | Per (%) | (NP) Respiration | (NP/NP+DP) R/R+P (%) | N-DO$^{14}$C | K[a] | Chl *a* | AR | $NO_3$-N[b] | $NH_3$-N[b] | $PO_4$-P[b] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Sargasso Sea* | | | | | | | | | | | | |
| 006 | 1.3 | ND | ND | 0.7 | 34 | −0.3 | 0 | 3.15 | 0.42 | 0.01 | 0.36 | 0.38 |
| 008 | 7.4 | ND | ND | 0.5 | 6 | 1.7 | 0.07 | 15.48 | 0.48 | 0.22 | 0.28 | 0.01 |
| 010 | 3.5 | ND | ND | 0.4 | 9 | 1.7 | 0.25 | 11.24 | 0.31 | 0.23 | 0.38 | 0.06 |
| | 4.1±3.1 | ND | ND | 0.5±0.2 | 16.3±15.4 | 1.0±1.2 | 0.11±0.13 | 9.96±6.26 | 0.40±0.09 | 0.15±0.12 | 0.34±0.05 | 0.15±0.20 |
| Caribbean | | | | | | | | | | | | |
| 012 | 19.2 | 0.6 | 3.1 | 3.9 | 17 | 1.9 | 0.44 | 18.31 | 1.05 | 0.05 | 0.02 | 0.02 |
| 013 | 40.1 | 1.5 | 3.6 | 5.3 | 12 | −0.5 | 0.27 | 19.45 | 2.06 | 0.04 | 0.14 | 0.04 |
| 014 | 26.2 | 1.6 | 5.9 | 3.7 | 12 | ND | 0.33 | 10.15 | 2.58 | 0.07 | 0.16 | 0.07 |
| 021 | 27.8 | ND | ND | 2.8 | 9 | ND | 0.34 | 25.17 | 1.10 | 1.18[c] | 0.24 | 0.07 |
| | 28.3±8.7 | 0.9±0.8 | 3.2±2.4 | 3.9±1.1 | 12.5±3.3 | 0.4±1.1 | 0.35±0.07 | 18.27±6.19 | 1.70±0.75 | 0.09±0.06 | 0.14±0.09 | 0.05±0.02 |
| *Peru* | | | | | | | | | | | | |
| 193 | 109.5 | 3.3 | 2.9 | 7.5 | 7 | 2.9 | 0.71 | 26.40 | 4.15 | 12.98 | 1.13 | 1.32 |
| 197 | 127.0 | 2.1 | 1.6 | 13.5 | 10 | 1.2 | 0.53 | 21.85 | 5.81 | 13.15 | 0.84 | 1.37 |
| 204 | 332.8 | 11.2 | 3.3 | 21.0 | 6 | −1.0 | 0.59 | 232.22 | 1.43 | 0.16 | 0.20 | 0.46 |
| 213 | 146.5 | 28.0 | 16.0 | 13.2 | 8 | 30.4 | 0.42 | 78.42 | 1.87 | 9.85 | 1.36 | 1.73 |
| 222 | 219.2 | 9.6 | 4.2 | 32.8 | 13 | 3.1 | 0.71 | 37.50 | 5.85 | 12.27 | 0.94 | 1.36 |
| 242 | 547.7 | 9.6 | 1.7 | 46.6 | 8 | 5.4 | 0.60 | 105.03 | 5.21 | 9.64 | 0.45 | 1.15 |
| 251 | 1311.7 | 24.6 | 1.8 | 197.9 | 13 | 2.5 | 0.67 | 277.85 | 4.61 | – | 0.07 | 1.74 |
| 278 | 216.3 | 31.9 | 12.9 | 23.5 | 10 | −4.6 | 0.24 | 58.08 | 3.72 | ND | 0.28 | 0.82 |
| 314 | 598.2 | 9.3 | 1.5 | 82.9 | 12 | 5.6 | 0.47 | 121.65 | 4.92 | 1.21 | 0.84 | 0.33 |
| 321 | 609.9 | 17.0 | 2.7 | 75.8 | 11 | −1.6 | 0.70 | 293.02 | 2.08 | 13.62 | 1.83 | 1.71 |
| 324 | 958.5 | 17.0 | 1.7 | 77.8 | 7 | 11.0 | 0.38 | 272.28 | 3.52 | 5.04 | 1.07 | 1.99 |
| 336 | 244.2 | 5.1 | 2.1 | 37.6 | 13 | 7.8 | 0.58 | 46.90 | 5.21 | – | 0.30 | 1.67 |
| | 451.8±373.5 | 14.1±9.8 | 4.4±4.8 | 52.5±52.9 | 9.8±2.6 | 5.2±9.0 | 0.55±0.15 | 130.93±106.83 | 4.03±1.54 | 7.79±5.65 | 0.78±0.53 | 1.30±0.53 |

[a] $K = 0.5\ (3.32/\Delta t) \log C_2/C_1$ (Walsh *et al.*, 1974) where $\Delta t$ = time and $C_1$ and $C_2$ are carbon fixation rates at 12 and 36 h

[b] Obtained from integrated euphotic zone nutrient concentration/depth of euphotic zone

[c] Average concentration in 100-11% depths (0 – 32 m)

[d] $NO_3$ concentrations in 100-11% light depths (0 – 10 m) were undetectable

Photosynthetic carbon declined during nocturnal incubations in the three environments from the Sargasso Sea to Peru. However, the variability was high in the 3 Sargasso Sea stations (006, 008, 010), with R/R+P ratios of 34, 6 and 9% for the stations. In the Caribbean, the respiratory demand resulted in nocturnal decreases of 9–17% of the daily productivity and a slightly lower range off Peru, 6–13%.

## Flux of DOM

The release of photosynthetic products ($DO^{14}C$) in the 3 areas followed the same trend as noted in productivities, with few detectable diurnal increases in the oligotrophic stations (006–021). Thus, extracellular release (PER) of $DO^{14}C$ in the Sargasso Sea was negligible and only 3.2% of total integrated diurnal productivity in the Caribbean (Table 2). In the eutrophic coastal waters of Peru, 14.1 mg C $m^{-2}$ $h^{-1}$ was released as $DO^{14}C$, comprising 4.4% of the total diurnal productivity. In general, diurnal production of $DO^{14}C$ exceeded nocturnal accumulation rates, particularly in the Peruvian stations (cf. D- and N-$DO^{14}C$, Table 2).

At discrete depths, the PER was usually similar to integrated values. However, in several stations, PER was elevated at the surface and 1% light level relative to other depths. For example, a PER of 20.8% was noted in surface samples at Station 193 while 24.5, 69.5 and 53.2% of the total carbon fixed was found as $DO^{14}C$ at the 1% light level at Stations 204, 213 and 278, respectively.

Few significant light-dependent changes in DOM were noted in the oligotrophic stations of the Sargasso Sea and the Caribbean (Table 3). Although DSAC concentrations remained relatively constant at most stations, significant diurnal increases in DSAC concentrations were noted only at Station 006, where the average rate of increase was 27.7 $\mu$g $l^{-1}$ $h^{-1}$ over the 9-h diurnal incubation period. Extracellular DFPA concentrations typically increased during diurnal incubations at all oligotrophic stations; the diurnal flux ranged from 9 to 230 ng DFPA $l^{-1}$ $h^{-1}$ with significant increases at Stations 006, 013 and 021. Nocturnal changes ranged from −124 to +16 ng DFPA $l^{-1}$ $h^{-1}$ (Table 3).

**Table 3.** Flux of DSAC and DFPA in the Sargasso Sea and Caribbean. D and N are diurnal and nocturnal sampling periods. $\Delta$ DSAC = $\mu$g DSAC $l^{-1}$ $h^{-1}$ and $\Delta$ DFPA = ng DFPA $l^{-1}$ $h^{-1}$, obtained from integrated flux/depth of euphotic zone (m). Significant (*) changes in concentration within each period were determined using the paired t-statistic, $\alpha = 0.05$. Integrated DSAC-flux data from Stations 012 and 013 not available (–)

| Station | Euphotic zone | $\Delta$ DSAC | | $\Delta$ DFPA | |
|---|---|---|---|---|---|
| | | D | N | D | N |
| 006 | 45 | 27.7* | −3.8 | 82.5* | −2.4 |
| 008 | 75 | 0.3 | 3.9 | 85.1 | −13.3 |
| 010 | 72 | 3.0 | 2.5 | 110.7 | 7.8 |
| 012 | 96 | – | – | 8.7 | −42.4* |
| 013 | 78 | – | – | 113.7* | −124.2 |
| 014 | 60 | 2.7 | 0.4 | 108.7 | 16.1 |
| 021 | 66 | 4.1 | 0.4 | 230.3* | −83.4 |

Strong diel cycles in the flux of DSAC and DFPA were observed off the coast of Peru, with increases in the dissolved pools apparently being light-dependent processes (Table 4). DSAC increased in 100% and DFPA in 75% of the diurnal incubations. In addition, no increases in DSAC and only one increase in DFPA were observed during the nocturnal incubations along the Peruvian coast. The average diurnal increases in the two DOM pools were 234 mg DSAC-C $m^{-2}$ $h^{-1}$ and 2.0 mg DFPA-C $m^{-2}$ $h^{-1}$ (assuming glycine as average amine) for the 12 Peruvian stations; nocturnal decomposition rates were 142 mg DSAC-C $m^{-2}$ $h^{-1}$ and 2.4 mg DFPA-C $m^{-2}$ $h^{-1}$, respectively.

In addition to the light-dependent accumulation of DSAC and DFPA in Peruvian waters, there was a strong relationship between productivity and the accumulation rates of extracellular organic matter. An increase in non-red tide phytoplankton productivity was accompanied by an increase in the DSAC and DFPA concentrations for all depths:

$$\text{mg DSAC-C } m^{-3}\ h^{-1} = 0.58\ (\text{total C fixed } m^{-3}\ h^{-1}) - 0.36 \quad (r^2 = 0.78;\ n = 57) \tag{1}$$

and

$$\text{mg DFPA-C } m^{-3}\ h^{-1} = 0.01\ (\text{total C fixed } m^{-3}\ h^{-1}) - 0.14 \quad (r^2 = 0.51;\ n = 57). \tag{2}$$

## Temporal Variability in DOM

To examine temporal variability in DOM, a fixed location off the Peruvian coast was sampled repeatedly (Stations 193–242) over an 8-d period. The concentrations of DSAC and DFPA changed markedly as different phytoplankton communities were encountered during the sampling period (Fig. 2). The communities on the first 2 sampling days were typified by a mixture of algal groups, including flagellates, diatoms and some ciliates (N. Ochoa, personal communication). Extracellular concentrations of DSAC were low, between 12.1 and 13.5 g DSAC $m^{-2}$ and fluctuated little over the incubation period. In ensuing days, diatoms dominated the waters. Initial concentrations of DOM increased, with pronounced light-dependent fluctuations observed. By the end of the sampling period, DSAC concentrations had increased to 42.6 g DSAC $m^{-2}$. DFPA concentrations also increased from 0.43 to 0.60 mg $m^{-2}$ over the same period.

## Heterotrophic Activity

Estimates of carbon flux in the DOM pool should give estimates of heterotrophic activity in the water column. Employing diurnal accumulation rates (P) as measures of

**Table 4.** Flux of DOM in Peruvian waters. A = autotrophic, P > R; H = heterotrophic, P < R where P = diurnal productivity, R = respiration

| Stn | Δ mg DSAC-C $m^{-2}$ $h^{-1}$ | | | Δ mg DFPA-C $m^{-2}$ $h^{-1}$ | | |
|---|---|---|---|---|---|---|
| | D Day | N Night | $\frac{D+N}{N}=\frac{P}{R}$ | D Day | N Night | $\frac{D+N}{N}=\frac{P}{R}$ |
| 193 | 5.6 | −5.4 | A | 0.80 | −0.25 | A |
| 197 | 0.5 | −2.5 | A | −4.12 | −3.47* | H |
| 204 | 187.6 | −234.5* | A | −3.47 | −2.04* | H |
| 213 | 10.5 | −58.4* | A | 1.90* | −1.69* | A |
| 222 | 131.1* | −95.0* | A | −0.30 | −1.13* | H |
| 242 | 402.6* | −248.4* | A | 1.64 | −2.63* | A |
| 251 | 582.3* | −168.9 | A | 19.91* | −9.30* | A |
| 278 | 195.6* | −63.7 | A | 0.14 | −0.96* | A |
| 314 | 520.0* | −368.3 | A | 1.54 | −2.96* | A |
| 321 | 166.9 | −263.6* | A | 2.65* | −2.13* | A |
| 324 | 503.1* | −183.9 | A | 1.78 | −2.68* | A |
| 336 | 102.2* | −5.9 | A | 1.35 | 0.05 | A |
| $\bar{x}_{12}$ | 234 | −142 | 2.65 | 1.99 | −2.43 | 1.82 |

* Significant at $\alpha = 0.05$, paired t-statistic of concentration changes per depth over time

(1) DSAC flux:

(a) Ratio of diurnal increases in DSAC to total diurnal incubations $= \frac{12}{12} \times 100 = 100\%$

(b) Ratio of nocturnal decreases in DSAC to total nocturnal incubations $= \frac{12}{12} \times 100 = 100\%$

(2) DFPA flux:

(a) Ratio of diurnal increases in DFPA to total diurnal incubations $= \frac{9}{12} \times 100 = 75\%$

(b) Ratio of nocturnal decreases in DFPA to total incubations $= \frac{11}{12} \times 100 = 92\%$

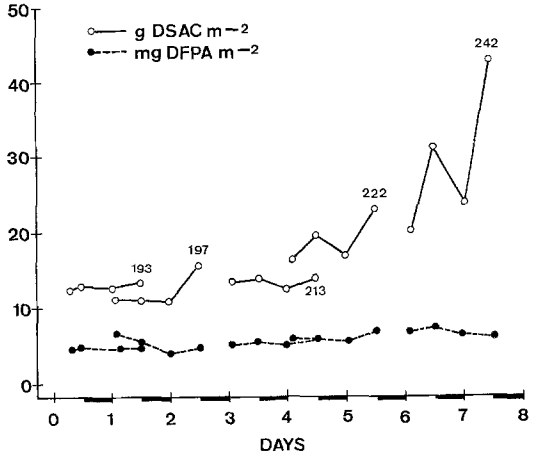


**Fig. 2.** The change in DSAC and DFPA over 8 d at the fixed location off the Peruvian coast (Stations 193–242). Each set of (connected) points represents the sample from each station. Individual points represent concentrations in sub-samples removed from each incubated sample initially, at sundown, sunrise and sundown the following day

autrophic activity and nocturnal decreases (R) in DOM for heterotrophic activity, P/R ratios were computed for coastal Peru. Average ratios were 2.65 for DSAC flux and 1.82 for DFPA.

## Red Tides

Red tides, large concentrations of the ciliate *Mesodinium rubrum*, were encountered in Peruvian coastal stations 194 and 204 A. The chlorophyll *a* concentrations were 162 and 229 $\mu g\ l^{-1}$, while carbon fixation rates were 1 815 mg C $m^{-3}$ [7.5 h]$^{-1}$ and 2 965 mg C $m^{-3}$ [5 h]$^{-1}$, respectively. Significant $DO^{14}C$ concentrations were found extracellularly amounting to 22.4 and 6.3% of the total carbon incorporated in the 2 stations (Table 5).

**Table 5.** Productivity and biomass in the 2 red tide stations, 194 and 204 A

| | Total | | |
|---|---|---|---|
| | Chlorophyll (mg $m^{-3}$) | Productivity (mg C $m^{-3}$) | PER (%) |
| 194 | 161.9 | 1 815 [7.5 h]$^{-1}$ | 22.4 |
| 204 A | 229.3 | 2 965 [5 h]$^{-1}$ | 6.3 |

## Discussion

### Phytoplankton Metabolism and Biomass

Phytoplankton productivity, respiration, release of $DO^{14}C$ and growth rates were estimated using classical $^{14}C$-procedures in the oligotrophic Sargasso Sea and Caribbean as well as the nutrient-rich, upwelling waters of Peru. Carbon fixation rates obtained in the blue water regions were similar to rates reported previously. Primary productivity was 43 mg C $m^{-2}$ $d^{-1}$, slightly less than the 0.05–0.46 g C $m^{-2}$ $d^{-1}$ range noted by Riley *et al.* (1949), Steemann-Nielsen (1952), Riley (1957), Menzel and Ryther (1960) and Carpenter and McCarthy (1975), for the Sargasso Sea. The average fixation rate for the Caribbean, 293 mg C $m^{-2}$ $d^{-1}$, was similar to rates noted by Burkholder *et al.* (1967) and Malone (1971) for surface waters near Puerto Rico and in the open Caribbean. Assimilation rates and growth rates also increased from the Sargasso Sea and Caribbean to coastal Peruvian waters. The Sargasso Sea phytoplankton communities divided 0.11 $d^{-1}$ with a low assimilation rate of 0.4 mg C mg chl $a^{-1}$ $h^{-1}$. Within the Caribbean, the assimilation rate increased to 1.7 mg C mg chl $a^{-1}$ $h^{-1}$ while the growth rate was 0.35 $d^{-1}$. These data would appear to indicate non-optimal conditions for phytoplankton growth and could result from chemical and/or biological control of productivity *in situ* (e.g. nutrient limitation) or possibly, incubation artifacts. The use of $^{14}C$-procedures and bottle incubations in oceanic areas for estimating primary productivity and, therefore, any associated physiological parameter (division rate, respiration, etc.) has been challenged recently, since bottle incubation may: (1) enhance zooplankton grazing success leading to $^{14}C$-fixation as a measure of standing crop (Sheldon and Sutcliffe, 1978); (2) underestimate primary productivity (Gieskes *et al.*, 1979; Postma and Rommets, 1979; Tijssen, 1979); (3) lead to reductions in chlorophyll concentrations (Gieskes *et al.*, 1979); and (4) result in a loss of phytoplankton cells (Venrick *et al.*, 1977). The contribution of such factors to these data was not determined during the present study and the data should be considered in this context. Since copepod grazing pressure was low in Peru (Dagg *et al.*, 1980), chlorophyll *a* concentrations high (130.9 $\mu g\ l^{-1}$) and the community dominated by diatoms, incubation artifacts common to oceanic systems may not be as important in limiting $^{14}C$-incorporation in the eutrophic upwelling samples. Average carbon fixation for the area was 4.8 g C $m^{-2}$ $d^{-1}$, falling within the range of values reported previously (Barber, 1967; Strickland *et al.*, 1969; Ryther *et al.*, 1971; Hobson *et al.*, 1973; Barber *et al.*, 1976, 1978; Sorokin and Mikheev, 1979). Growth rates and assimilation rates were 0.55 divisions $d^{-1}$ and 4.0 mg C mg chl $a^{-1}$ $h^{-1}$, respectively, for the upwelling phytoplankton communities; ambient inorganic nutrient concentrations were high, with > 8 mg-at N $m^{-2}$ in the euphotic zone. These data indicate relatively good conditions for phytoplankton growth were present, which was not surprising considering low grazing pressure and a continuous, abundant supply of inorganic nutrients in the upwelled waters.

### Phytoplankton Respiration

The nocturnal carbon fixation rates noted in the present study indicated relatively constant respiration rates for oligotrophic and eutrophic phytoplankton communities. Respiration/gross photosynthesis was 16.3 ± 15.4%, 12.5 ± 3.3% and 9.8 ± 2.6% in the Sargasso Sea, the Caribbean and Peru, respectively. The relatively constant rate in oligotrophic and eutrophic areas agrees with the observations of Steemann-Nielsen and Hansen (1959) for coastal and oceanic phytoplankton communities of the North Atlantic and is less than the 50% noted in the North Pacific (Eppley and Sharp, 1976) and 30% in the Gulf of Maine (Mague *et al.*, 1980). Estimates of phytoplankton respiration in diatom-dominated areas of Peru and N. W. Africa have been obtained from $^{14}C$-techniques and electron transport system-procedures, with respiration consuming 7.8–14% of total particulate production (Smith, 1977; Packard, 1979; Setchell and Packard, 1979; Smith and Barber, 1979b). Thus, in eutrophic areas, generally 10–15% of total photosynthetic production is consumed in respiratory metabolism. If the $^{14}C$-fixation rates for the oligotrophic stations actually simulate field activity in the present study, phytoplankton respiration may be a similar percentage of total photosynthesis in all environments. Since respiration/photosynthesis approaches unity in nutrient-starved or senescent phytoplankton cultures (Ryther, 1954, 1956a, b; Sharp *et al.*, 1980), a constant low respiration/photosynthesis ratio implies that oligotrophic phytoplankton communities must be growing near $\mu_{max}$ (Goldman *et al.*, 1979), perhaps a slower $\mu_{max}$ evolved over time, as proposed by Jackson (1980). However, the oligotrophic $^{14}C$-fixation rates used to calculate respiration rates might suffer from a variety of incubation artifacts previously discussed. Therefore, the respiration rates for the oligotrophic areas should be accepted with similar limitations ascribed to the diurnal productivities and division rates.

### Flux of $DO^{14}C$, DSAC and DFPA

The dissolved organic carbon released from marine phytoplankton appears to be a relatively small percentage of total productivity (Williams and Yentsch, 1976; Sharp, 1977; Mague *et al.*, 1980). In the present study, all three areas were typified by the release of small portions of recent photosynthate with undetectable quantities noted in the Sargasso Sea, 3.2% in the Caribbean and 4.4% in Peru. If phytoplankton communities in the Sargasso Sea had been releasing > 30% of total productivity as noted in previous oligotrophic communities (Anderson and Zeutschel, 1970; Thomas, 1971; Choi, 1972), increases in the $DO^{14}C$ pool would have been detectable in filtrate activity (cpm). Release of $DO^{14}C$ must be less than this estimate and

therefore, high PER were not recorded for this area. Hobbie *et al.* (1972) recorded a mean PER (± SD) from the western Sargasso Sea of 23 ± 15% for 13 depths; however, the DO$^{14}$C concentrations were very low, possibly not significantly different from zero. In contrast to the data of Hobbie and co-workers, Williams and Yentsch (1976) recorded an average PER of 6.9% for phytoplankton collected near the Bahamas. The low values recorded in the oligotrophic regions indicate either relatively healthy cells in these areas, as higher relative release rates have been reported for stationary growth phase (Thomas, 1964; Eppley and Sloan, 1965), or rapid uptake of the released products by the heterotrophic bacterioplankton. The latter process is unlikely, however, as bacteria in open ocean waters are probably in a stationary phase of growth, implied from an adenylate energy charge of 0.6 (Wiebe and Bancroft, 1975) and the predominance of coccoid bacterial forms (Wiebe and Pomeroy, 1972). Since coccoid forms have been implicated as resting stages during starvation conditions (Novitsky and Morita, 1978), rapid bacterial uptake of DO$^{14}$C seems unlikely.

In general, accumulation of DO$^{14}$C was greater in diurnal incubations, but did persist in the nocturnal periods. Diurnal increases in DO$^{14}$C, particularly evident off Peru, probably indicate light-mediated production of photosynthetic products with release declining as intracellular pools decrease during the dark period (Mague *et al.*, 1980).

The carbon released as DO$^{14}$C and as DSAC-C during diurnal incubations differed substantially, with the average increase of DSAC-C (234 mg C m$^{-2}$ h$^{-1}$) exceeding DO$^{14}$C produced (14.1 mg C m$^{-2}$ h$^{-1}$) by 17-fold. This discrepancy is difficult to explain, particularly since both DOM pools were light-dependent processes and directly related to primary productivity. Concentrations of DOM were not found to be significantly changed by microzooplankton grazing or otherwise associated with zooplankton abundance (Cota *et al.*, 1980) and in addition, grazing effects would not be light-dependent. One possible explanation concerns intracellular isotopic disequilibrium between $^{14}$C and $^{12}$C. Storch and Saunders (1978) noted total extracellular DOC accumulation could be underestimated by 4- to 6-fold, depending on the $^{14}$C/$^{12}$C ratio within the phytoplankton cells. Similarly, synthesis of small monosaccharides within the phytoplankton should occur very rapidly while polymerization of the monosaccharides into heteropolysaccharides typical of diatom wall material (Smestad *et al.*, 1974; Brockmann *et al.*, 1979; Percival *et al.*, 1980) should require longer periods. If the extracellular DSAC increase was polysaccharide material as noted in diatom laboratory cultures (Handa, 1970; Myklestad and Haug, 1972; Myklestad *et al.*, 1972; Myklestad, 1974; Haug and Myklestad, 1976; Sellner, 1978), it is conceivable some lag should be found between extracellular accumulation of cold-polysaccharides and $^{14}$C-labeled polysaccharide in the Peruvian stations, as suggested by Mague and co-workers (1980). The total DSAC concentrations measured during diurnal incubation in the present study would include both pools, while the DO$^{14}$C data would only include low molecular weight, rapidly labeled compounds and polysaccharides formed from polymerization of labeled monosaccharides. A lag in the production of DO$^{14}$C in phytoplankton has been noted previously (Lancelot, 1979) with Mague and co-workers (1980) effectively summarizing this problem when discussing extracellular release of DO$^{14}$C in a several-hour experiment. They state that, "The time required for radioisotopic equilibration of these substances (polysaccharides, soluble enzymes, cell-surface materials) would be quite long ... and ... [the $^{14}$C data] would not have accounted for such a release of unlabeled organic carbon." However, it is difficult to imagine that "any" lag could account for the 17-fold difference in carbon in the two pools. Future work is required to fractionate the extracellular and intracellular carbon compounds before this large difference may be explained.

The light-dependent accumulation of DO$^{14}$C, DSAC (Peru) and DFPA (all 3 areas) coupled with the strong correlation (Peru) of diurnal increases in DSAC and DFPA with total productivity suggest that phytoplankton were the source of the large DOM pool. Diurnal accumulations of DSAC have also been attributed to phytoplankton in other aquatic systems (Walsh, 1965; Brockmann *et al.*, 1979) and in laboratory diatom cultures, extracellular polysaccharides are common by-products of diatom growth (e.g. see results of Myklestad and co-workers). The predominance of diatoms in days 5 and 6 in the fixed Peruvian stations was associated with the highest DSAC

**Table 6.** A comparison of intracellular and extracellular saccharide (SAC) carbon in diurnal incubations in Peruvian neritic waters

| Stn | Intracellular[a] SAC-C productivity 12 h$^{-1}$ | Initial[b] intracellular SAC-C | Total intracellular[c] SAC-C in diurnal incubation | Total extracellular[d] DSAC-C accumulation during diurnal incubation |
|---|---|---|---|---|
| 193 | 459.6 | 582.1 | 1 041.7 | 67.2 |
| 197 | 534.0 | 481.8 | 1 015.8 | 6.0 |
| 204 | 1 398.0 | 5 120.5 | 6 518.5 | 2 251.2 |
| 213 | 615.6 | 1 729.2 | 2 344.8 | 126.0 |
| 222 | 920.4 | 826.9 | 1 747.3 | 1 573.2 |
| 242 | 2 300.4 | 2 315.9 | 4 616.3 | 4 831.2 |
| 251 | 5 509.2 | 6 126.6 | 11 635.8 | 6 987.6 |
| 278 | 908.4 | 1 280.7 | 2 189.1 | 2 347.2 |
| 314 | 2 512.8 | 2 682.4 | 5 195.2 | 6 240.0 |
| 321 | 2 562.0 | 6 461.1 | 9 023.1 | 2 002.8 |
| 324 | 4 026.0 | 6 003.8 | 10 029.8 | 6 037.2 |
| 336 | 1 026.0 | 1 034.2 | 2 060.2 | 1 226.4 |

[a] Calculated from (particulate productivity) (12 h) (0.35) = mg SAC-C m$^{-2}$ 12 h$^{-1}$

[b] Calculated from (0.35) (chlorophyll) (63 C chlorophyll$^{-1}$) = mg SAC-C m$^{-2}$. C/chl ratio of 63 obtained from Harrison and Platt, unpublished data

[c] Calculated from a + b = mg SAC-C m$^{-2}$

[d] Mg DSAC-C m$^{-2}$ 12 h$^{-1}$

accumulation rates (131 and 403 mg DSAC-C $m^{-2} h^{-1}$, respectively) for the 8-d period, indicating the other phytoplankton species may not have released large quantities of extracellular saccharide.

Assuming phytoplankton to be the sole source of DSAC in Peruvian waters leaves some results unexplained, however. The 17-fold discrepancy between DSAC-C and $DO^{14}C$ in the diurnal incubations discourages the sole-source theory. Further, although light-mediated DSAC accumulation and correlation of DSAC accumulation with total productivity imply phytoplankton as producers, extracellular saccharide pools exceeded cellular saccharide pools during diurnal incubations in Peruvian Stations 242, 278 and 314 (Table 6). These results could be explained by: (1) a light-dependent source of DSAC other than phytoplankton; (2) underestimates of initial intracellular carbohydrate concentrations; (3) underestimates of primary productivity and hence diurnal increases in intracellular carbohydrate, or (4) overestimates of extracellular saccharide concentrations. Unfortunately, data supporting any of these explanations are not available from the present study and until these questions are resolved, phytoplankton must be accepted as the source of DOM off Peru.

Heterotrophic utilization of DSAC (7 $\mu$g DSAC-C $l^{-1} h^{-1}$) was less than the diurnal accumulation rate (11 $\mu$g DSAC-C $l^{-1} h^{-1}$), resulting in a net accumulation of DSAC in the Peruvian waters (see Table 4). In contrast, the net flux of DFPA was zero, as diurnal accumulation rates were similar to nocturnal reduction rates (2 mg DFPA-C $m^{-2} h^{-1}$, assuming the molecular weight of glycine as the average amine molecular weight). Zero net flux of DFPA is not surprising, considering amines contain N and C for the heterotrophic flora and are preferred substrates for bacterial uptake. Seeding of offshore waters with these organic nitrogen compounds is not likely as turnover appeared to be rapid ($\leqq$ 24 h). The predominance of autotrophic production over heterotropic utilization of DOM off Peru was evident, with P/R ratios usually greater than 1 (noted in Table 4). As an index of total plankton carbon flux, the ratios indicate production of DOM exceeds utilization in the euphotic zone waters, supporting the contention that a net accumulation of DOM would result in these waters.

Diel cycles of DOM in other systems also indicate net accumulation. Diurnal increases in dissolved saccharides were 88 $\mu$g DSAC-C $l^{-1} h^{-1}$ for a coastal tidal pond (Walsh, 1965), approximately 4.1 $\mu$g DSAC-C $l^{-1} h^{-1}$ for inshore waters of the southern North Sea (Brockmann *et al.*, 1979) and 11 $\mu$g DSAC-C $l^{-1} h^{-1}$ for coastal Peruvian waters (present study). Nocturnal losses were 50, 4 and 7 $\mu$g DSAC-C $l^{-1} h^{-1}$ for the same areas, respectively. Burney *et al.* (1979) reported DSAC-C disappearance at 5 $\mu$g C $l^{-1} h^{-1}$ for the North Atlantic. The decrease of amine carbon in the present study (0.1 $\mu$g DFPA-C $l^{-1} h^{-1}$) was similar to rates reported previously in other marine areas (Crawford *et al.*, 1974; Williams *et al.*, 1976; Gocke, 1977; Brockmann *et al.*, 1979).

## Heterotrophic Activity

The flux of DOM can be used to estimate bacterial production in Peruvian waters. Drastically different results were obtained using the $DO^{14}C$ and DSAC data, since the latter rates formed greater than 50% of the total productivity (see Eq. 1). Employing dark $DO^{14}C$ release values of 0.15–0.475 times the light release rates (Smith *et al.*, 1977), minimum and maximum rates of heterotrophic uptake can be calculated from diel changes in the $DO^{14}C$ pool. Bacterial heterotrophic rates ($\pm$ 1 SD) range from 0–462 mg C $m^{-2}$ [24 h]$^{-1}$, or 0–9% of total daily photosynthesis. If bacterial assimilation efficiencies are assumed to be 50%, 0–231 mg bacterial-C $m^{-2}$ will be synthesized each day. Using the DSAC data and assuming no nocturnal release of DSAC, bacterial heterotrophy for a 20 m water column averages 3.41 g C $m^{-2} d^{-1}$, 85% of total daily productivity, resulting in an increase of bacterial carbon of 1.7 g C $m^{-2} d^{-1}$. Since bacterial biomass in the euphotic zone for all Peruvian stations ranged from 200–500 mg C $m^{-2}$ (Hendrikson *et al.*, submitted), division rates for the bacterial community can be calculated from $K = 3.32 \log \frac{B+B'}{B}$, where K is divisions $d^{-1}$, B is initial biomass (mg C $m^{-2}$) and B′ is the rate of increase $d^{-1}$. Bacterial growth rates for $DO^{14}C$ flux (max.) and DSAC flux are 0.73 and 2.81 div $d^{-1}$, respectively, assuming an average bacterial biomass of 350 mg C $m^{-2}$. Since bacterial doubling time in coastal waters (J. A. Fuhrman, personal communication; Hagström *et al.*, 1979; Fuhrman and Azam, 1980) or open-ocean waters (Sieburth *et al.*, 1977; Karl, 1979) can be several hours, the rate calculated from the DSAC data may not be unrealistic, whereas the rate derived from the $DO^{14}C$ data may represent a minimum estimate. Therefore, as a percentage of autotrophic production, bacterial production estimates from the flux of DSAC in these studies exceed the rates for this area estimated by $DO^{14}C$ reported by Smith and Barber (1979b) by approximately 10- to 20-fold. It should be noted that this is the same order of magnitude difference observed between $DO^{14}C$ and DSAC accumulation rates.

## Red Tides

The carbon fixation rates for the *Mesodinium rubrum* populations were high but probably represent minimum estimates. Smith and Barber (1979a) noted incubations exceeding 1–2 h resulted in cell lysis of this fragile species. In the present study, red pigment was observed on several filters, indicating lysis and increased concentrations of DOM from intracellular material passing the filter. This could certainly account for the 22.4% release noted at Station 194. Large increases in DSAC and DFPA were also observed during the diurnal incubation; however, due to cell lysis, these data were not presented. Even as minimum estimates, the carbon fixation rates noted off Peru indicate

red tides may provide large aperiodic pulses of particulate and dissolved organic matter to the Peruvian shelf. It would be interesting to determine the temporal and spatial frequency of the red tides to determine their quantitative role in shelf energetics.

## Carbon Flux: Labeled and Unlabeled Carbon Pools

As mentioned prevously, there has been increasing debate in recent years over the estimates of primary productivity obtained from the $^{14}C$-technique. The most recent direct challenge to the $^{14}C$-technique arose from the comparative research programs of the Dutch scientists in the equatorial North Atlantic (Gieskes *et al.,* 1979; Postma and Rommets, 1979; Tijssen, 1979). The results indicated $^{14}C$-productivities could underestimate gross photosynthesis by up to 10–20 times.

In the present study, long term incubations (48 h) were employed in order to estimate phytoplankton growth rates. Since incubations in containers suffer from a variety of artifacts previously noted, it is highly likely that estimates of phytoplankton metabolism, including productivity, respiration, assimilation ratios and division rates, would be underestimated in the present study. Thus, growth rate calculations (Table 2) would be underestimates of rates *in situ.* In addition, any ratio involving these physiological parameters (e.g. DSAC/total productivity) would be overestimates. It should be noted that PER did not increase with incubation time, indicating that cells initially fixing carbon were not lysing over the incubation period.

Since changes in DSAC or DFPA included labeled and non-labeled compounds, carbon flux from those pools would be expected to be greater than measured with the labeled isotope; hence, greater carbon flux in DSAC than in $DO^{14}C$ was not unexpected. However, the magnitude of the difference was not anticipated. This large difference would also be reflected in calculations of bacterial growth rates employing the $DO^{14}C$ and DSAC data. Further, little carbon flux through the bacteria would be expected using $DO^{14}C$ as the substrate, as was found in N. W. Africa (Smith *et al.,* 1977) and Peru (Smith and Barber, 1979 b; present study).

General, non-radiosotopic analytical techniques in other studies have yielded similarly high carbon flux rates. For example, Walsh (1965) observed diurnal increases in dissolved carbohydrates in a coastal tidal pond which averaged 88 $\mu g\ C\ l^{-1}\ h^{-1}$ while nocturnal decreases averaged 50 $\mu g\ C\ l^{-1}\ h^{-1}$. In the North Atlantic, Burney and co-workers (1979) noted decreases in DSAC pools of 5 $\mu g\ C\ l^{-1}\ h^{-1}$. High flux rates have also been observed for dissolved amines in marine areas. Using high pressure liquid chromatographic techniques, Mopper and Lindroth (in press) noted dissolved free amino acids decreased at approximately 2 $\mu g\ C\ l^{-1}\ h^{-1}$ in the upper 60 m of the Baltic Sea. These rates for DSAC and dissolved amines exceed maximum uptake rates ($V_{max}$) collected with radioisotopic compounds by one to several orders of magnitude (see Table 1, Hoppe (1978) for comparison). Carbon budgets prepared from these data will consequently be much lower than recorded for the total labile fractions.

Future work on carbon flux through the lower trophic levels should include simultaneous measurements of POC, $PO^{14}C$, DOC and $DO^{14}C$, permitting identification of temporal changes in specific activities of individual fractions or compounds in each fraction. Although several studies exist documenting labeling patterns in phytoplankton populations (Morris *et al.,* 1974; Hitchcock, 1978), time course changes on specific activities of extracellular organic matter and wall materials were not determined. If $DO^{14}C$ release underestimates total release of organic carbon by up to 4- to 6-fold in photosynthesizing phytoplankton (Storch and Saunders, 1978), changes in specific activities of released organic matter are essential in more precise estimates of total productivity.

In summary, it appears phytoplankton may be responsible for a majority of the extracellular carbon observed in eutrophic marine areas. Extracellular accumulations of $DO^{14}C$, DSAC and DFPA were light-dependent processes, with a strong correlation between diurnal increases in DSAC and DFPA and total phytoplankton productivity. Accumulation rates exceeded decomposition rates of DSAC; diatoms appeared to be the major producers of the DSAC.

In oligotrophic areas, DSAC flux was difficult to establish, probably due to the small changes in DSAC concentrations approaching the analytical sensitivity of the methods; diurnal incubations were typified by increases in DFPA concentrations. Future research should attempt to resolve the discrepancies between carbon flux in $PO^{14}C$, $DO^{14}C$ and POC, DSAC pools.

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