

The distribution and biochemical composition of biogenic particles across the subtropical Front in June 1993 (Azores-Madeira region, Northeast Atlantic)*

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SUMMARY: Water samples were collected in the north-east Atlantic Ocean between the Azores and Madeira (33°N-36°N and 24°W-26°W) during the Oceanographic Cruise SEMAPHORE in June 1993. Temperature, salinity, nutrients (nitrate and phosphate) and particulate organic matter (organic carbon, organic nitrogen, carbohydrates, proteins and phytopigment) were investigated in the water column to a depth of 2000 m. The presence of the subtropical front (STF) separating warmer more saline Western Atlantic Water (WAW) from colder and fresher Eastern Atlantic Water (EAW) in the upper 100 m, and a tongue of salt water arising from the influence of Mediterranean Water (MW) at a depth of 1000 m, were well identified by the physical and chemical parameters. POC and PON concentrations, in the surface layer (0-100 m), ranged between 23.3-64.5 and 2.9-9.1 $\mu\text{g l}^{-1}$ respectively, while concentration between 12.4-30.5 and 1.1-4.0 $\mu\text{g l}^{-1}$ prevailed below the thermocline (100-2000 m). The very low POC and PON concentrations together with the low nutrient and chlorophyll-a concentrations confirmed the oligotrophic nature of the Azores-Madeira region. Statistical analysis was carried out to investigate the difference in the quantity and quality of POM between water masses. Regression analysis showed a high correlation between POC and PON but the slopes and intercepts of the regression lines did not differ significantly between WAW and EAW. In contrast, an examination of vertical profiles as well as mean integrated values of biochemical variables in the upper 100 m suggest a difference in the quantity and quality of biogenic particles between the water masses. WAW showed the lowest integrated concentrations of particulate organic carbon, particulate organic nitrogen, particulate protein and particulate carbohydrate. In contrast, frontal stations showed the highest values while EAW stations showed intermediate values. All these results, coupled with the occurrence of the highest POC:Chl-a ratio in EAW, suggest a temporal offset in the production cycle between the two water masses. Alternatively, the WAW is a more stratified and oligotrophic body of water than is EAW, and it always has lower biomass and nutrients than the more productive EAW. High chlorophyll-a concentrations were linked to the STF; moreover the average depth of the subsurface chlorophyll maximum (DCM) appeared to shift to shallower values at the frontal stations, suggesting a close association between the STF-Azores Current (AC) physical structure and the distribution of chlorophyll-a in this area.

Key words: Subtropical Front; Particulate Organic Matter; North Atlantic Ocean.

RESUMEN: DISTRIBUCIÓN Y COMPOSICIÓN BIOQUÍMICA DE PARTÍCULAS BIOGÉNICAS A TRAVÉS DEL FRENTE SUBTROPICAL DURANTE JUNIO DE 1993 (REGIÓN DE AZORES-MADEIRA, ATLÁNTICO NOR-ORIENTAL). – Se recogieron muestras de agua del Océano Atlántico Nor-Oriental entre Azores y Madeira (33°N-26°N y 24°W-26°W) durante la Campaña Oceanográfica SEMAPHORE en Junio de 1993. Se determinó la temperatura, salinidad, nutrientes (nitrato y fosfato) y materia orgánica particulada (carbono y nitrógeno orgánicos, carbohidratos, proteínas y fitopigmentos) en la columna de agua hasta una profundidad de 2000 m. La presencia de un Frente Subtropical (STF) que separaba aguas occidentales Atlánticas (WAW) más templadas y salinas de aguas Atlánticas orientales (EAW) más frías por encima de los 100 m, y la aparición de una lengua de agua más salada debida la influencia de aguas del Mediterráneo (MW) a la profundidad de 1000 m eran identificadas por parámetros físicos y químicos. Las concentraciones de POC (carbono orgánico particulado) y PON (nitrógeno orgánico particulado) en la capa superficial (0-100 m) oscilaban, respectivamente, entre 23.3-64.5 y 2.9-9.1 $\mu\text{g l}^{-1}$, mientras que concentraciones entre 12.4-30.5 y 1.1-4.0 $\mu\text{g l}^{-1}$ son las que prevalecían a profundidades por debajo de la termoclina (100-2000 m).

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Las bajas concentraciones de POC y PON junto con las bajas concentración de nutrientes y clorofila-a, confirmaban el carácter oligotrófico de la región Azores-Madeira. El análisis estadístico fue llevado a cabo para investigar las diferencias en cantidad y calidad de la POM (materia orgánica particulada) entre masas de agua. El análisis de regresión mostraba una alta correlación entre POC y PON pero las pendientes y los interceptos de las rectas de regresión no diferían significativamente entre WAW y EAW. Sin embargo, si se examinaban los perfiles verticales así como los valores medios integrados de las variables bioquímicas por encima de los 100 m se percibía una cierta diferencia en la cantidad y calidad de las partículas biogénicas entre las masas de agua. Las aguas occidentales Atlánticas (WAW) mostraban valores de concentraciones integrados más bajos en carbono orgánico particulado, nitrógeno orgánico particulado, proteínas y carbohidatos particulados. En cambio las estaciones del Frente presentaban los valores más elevados, mientras que las estaciones de EAW mostraban valores intermedios. Todos estos resultados, ligan con el hecho de la aparición de los cocientes POC:chl a más elevados en las aguas Atlánticas orientales (EAW), lo que sugiere una compensación en el ciclo de producción entre las dos masas de agua. Alternativamente, las WAW constituyen una masa de agua más estratificada y oligotrófica que las de EAW y siempre con menor biomasa y nutrientes que las EAW más productivas. Las altas concentraciones de clorofila-a estaban ligadas al STF; además la profundidad media de la capa subsuperficial del máximo de clorofila (SCM) cambiaba a valores menos profundos en las estaciones del frente, indicando una estrecha asociación entre la estructura física de STF- corriente de Azores y la distribución de la clorofila-a en dicha área.

Palabras clave: Frente Subtropical, materia orgánica particulada, Océano Atlántico Nor-Oriental.

INTRODUCTION

Frontal systems are hydrodynamic features that separate water masses with different thermohaline characteristics and in which the spatial-temporal scales at which physical forces operate are in resonance with the scale relevant for biological processes (Legendre *et al.*, 1986).

Previous studies suggest increased chlorophyll concentrations and pelagic primary production in such areas (Riegman *et al.* 1990, Heilmann *et al.* 1994) as well as changes in pelagic community structure (Lindley and Williams, 1994). Extensive work on the coupling between physics and biology in frontal systems has been carried out in coastal marine environments (e.g. Houghton and Marra, 1983; Holligan *et al.*, 1984; Kiorboe *et al.*, 1988) and also in oceanic fronts associated with the Gulf Stream (e.g. Hitchcock *et al.*, 1993; Lohrenz *et al.*, 1993). Among large-scale fronts, subtropical fronts are important both because of their large spatial extent and temporal persistence and because jet-like flows associated with them (Sverdrup *et al.*, 1942) are known to generate highly dynamic systems where strong biological responses are likely to occur (Fasham *et al.*, 1985; Pak *et al.*, 1988).

Particulate organic matter (POM) is of considerable biogeochemical and oceanographic importance, representing a carrier for transport of chemical elements from surface waters of the ocean to the sediments. POM distribution may be affected by local input and transport via gravitational settling, advection, diffusion as well as resuspension from bottom sediments (Fabiano *et al.*, 1993).

Most biogenic particles originate in the ocean photic layer (Eppley and Peterson, 1979). Variations in POM composition can arise from a number of factors, including phytoplankton populations with

varying constituent ratios (Fichez, 1991; Navarro *et al.*, 1993; Fabiano *et al.*, 1998). Particle settling through the water column is coupled with biochemical changes and nutrient enrichment of the deep waters (Angel, 1989; Fabiano *et al.*, 1998-2000). The labile fraction of POM, mostly derived from phytoplankton, is composed essentially of proteins, carbohydrates and lipids (Poulet *et al.*, 1986; Fabiano *et al.*, 1993).

The particulate organic matter of the Atlantic Ocean waters was studied in the 1960's (e.g. Wankersky and Gordon, 1965; Menzel, 1967; Gordon, 1970) and there has been growing interest in recent years due to its importance for the study and the understanding of global biogeochemical cycles (e.g. Jahnke, 1996; Boyd and Newton, 1999; Körtzinger *et al.*, 2001).

In the present study the biochemical composition and spatial distribution of POM were investigated across the subtropical front (STF) southwest of the Azores. The STF separate warmer more saline Western Atlantic Water (WAW) from colder and fresher Eastern Atlantic Water (EAW).

Previous investigations carried out in this area found a link between the presence of the STF and the quantity and quality of POM in the different water masses. Fernandez *et al.* (1996) in March 1992 observed a coupling between the STF-AC physical feature and high levels of chlorophyll-a. Primary production rates measured in the frontal high chlorophyll region ($> 1 \text{ mg C m}^{-3} \text{ h}^{-1}$) were much higher than previous measurements carried out in the same area in late spring and summer and about 2-times higher than modelling estimates for the region (Fernandez and Pingree, 1996). Later in the season (April-May 1981), Fasham *et al.* (1985) observed the presence of a well established deep chlorophyll maximum (DCM) but little evidence

was found for an increased phytoplankton biomass associated with the front. In the same work, the DCM in WAW was on average 20 m deeper and between 50% and 60% of the magnitude of that in EAW. This was explained by the authors by assuming an overall lower level of nutrients and primary productivity in WAW (Fasham *et al.*, 1985).

The aims of this research were: (i) to investigate the location and spatial extension of the subtropical front in June 1993, (ii) to describe the biochemical composition and spatial distribution of POM across the STF in the Azores Madeira region, and (iii) to study the association between the STF-AC physical structure and the biological processes occurring in the area.

MATERIAL AND METHODS

Area description and sampling

During summer 1993 an oceanographic cruise took place within the experimental framework of the 'Structure des Echanges Mer-Atmosphere, Proprietes des Heterogeneites Oceaniques: Recherche Experimentale' (SEMAPHORE), from 22st June to 4th July, in the northern Canary Basin. The water circulation in this region is well studied (Sy, 1988; Pollard *et al.*, 1996; Castro *et al.*, 1998). The Azores Current (AC) is the south-east extension of the Gulf Stream (Gould, 1985). This current joins together with the Portugal Current to the south and then becomes part of the North Equatorial Current that

flows to the west (Kase and Siedler, 1982). Gould (1985) maintains that the thermohaline Azores Front observed by Kase and Siedler (1982) is limited in the south by Mediterranean waters; in our study region, the influence of the Mediterranean zone is important. The mixed layer is maximum (~200 m depth) in winter and minimum (~50 m depth) in summer (Levitus, 1982). Below this layer, the North Atlantic Central Water (NACW) occurs at ~500-600 m, NACW is underlain by intermediate waters (Worthington, 1976; Kase *et al.*, 1985) with the Mediterranean waters, characterised by higher temperature and salinity between ~ 800-1300 m. Middle NADW occurs at ~2000 m depth and below 3000 m there is the Lower NADW that arises from the mixing of the waters of the Norwegian Sea and the Denmark Strait (Kawase and Sarmiento, 1986).

During June 1993, twelve stations were sampled between 33°N-36°N and 24°W-26°W (Fig. 1) on board the R/V Alliance (SACLANTCEN, La Spezia, Italy). Water sampling was carried out by means of 10-liter Niskin bottles assembled in a rosette-sampler or mounted on hydrographic wire. In the upper 2000 m, nominal sampling depths were: the surface (conventionally indicated from now on: 0 m), 10, 25, 50, 75, 100, 150, 300, 500, 700, 1000, 1500 and 2000 m.

Methodologies and instruments

The hydrological casts were supported by a CTD vertical profile recorded from either EG + G Mk3 or ME mod KMS probes. Temperature and depth were

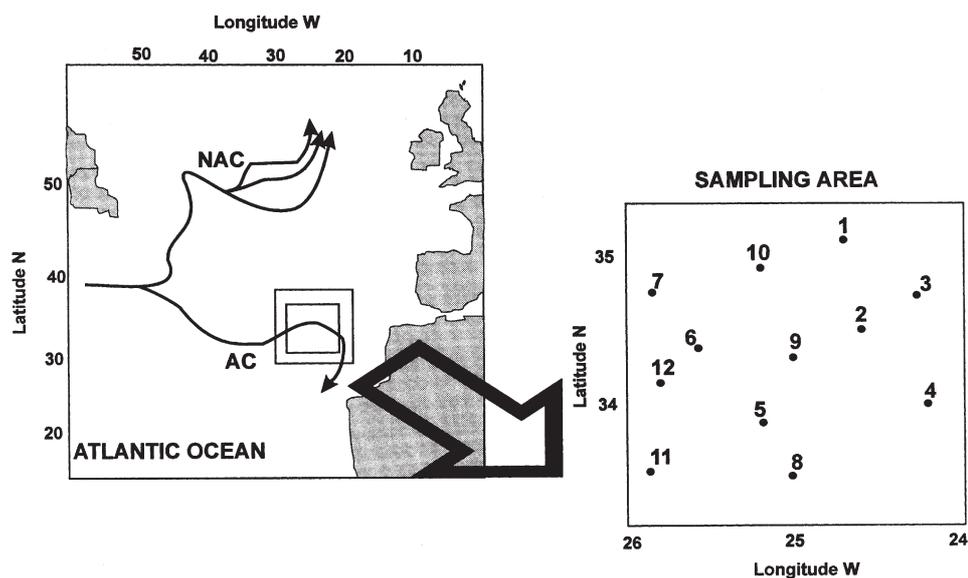


FIG. 1. – The location of sampling stations in the SEMAPHORE area between 33°N-36°N and 24°W-26° W southwest of Azores (AC: Azores current, NAC: North Atlantic Current).

checked by means of analogue or SIS digital reversing thermometers and pressure-meters, placed on the Niskin bottles. At the same time, salinity samples were collected at discrete depths to compare continuous vertical profiles with the values obtained by Autosal 8400 Guildline or Minisal 2001 AGE salinometers.

Chemical analysis was carried out on board; nutrients were assessed according to Hansen and Grasshoff (1983) using a Technicon II autoanalyzer.

Water samples (0.5-2.0 l), for particulate organic matter analysis, were prefiltered on 200 μm mesh net to retain larger particles and then filtered. Nuclepore filters (0.4 μm pore size) were utilized for chlorophyll-a (Chl-a), phaeopigment (PHAEO), particulate protein (PPRT) and particulate carbohydrate (PCHO) determination, combusted Whatman GF/F filters (0.8 μm pore size) were used for organic carbon (POC) and nitrogen (PON) analyses. Filters were then stored at -20°C . Since we used different types of filters for the protein (nuclepore) and PON (GF/F) analyses, a problem arised with protein-N to particulate nitrogen ratio (exceeding one). For these reason, we avoid the analysis of the two parameters in a single task or in quantitative terms because it is in our understanding this might probably lead to an uncorrected interpretation of the aliased data. In contrast we only used PPRT and PON data in relation to parameters such as POC, PCHO and Chl-a data for the calculation of the C/N, PPRT/PCHO and Chl-a:PPRT ratios as tools to assess qualitative aspect of particulate matter. The problem does not arise when using POC and PON versus Chl-a data (such as the use of POC:Chl-a ratios) given the size of phytoplankton cells normally exceeds 0.8 μm .

Samples were collected on single replicates. However, a series of replicate samples (3 to 5) were collected at different times on surface water in the Canary basin to define the coefficient of variations (C.V.) for the various parameters. C.V.s were: 5.3% for POC, 5.7% for PON, 16% for PCHO and 8.2% for PPRT.

Chlorophyll-a and phaeopigment (90% acetone extraction) concentrations were determined spectrophotometrically according to Lorenzen and Jeffrey (1980). Phaeopigments were measured after acidification of the supernatant with 0.1N HCl. Particulate carbohydrates were measured according to Dubois *et al.* (1956). D(+)-glucose was used as a standard. Particulate proteins were assessed according to Hartree (1972) with bovine albumine solutions used as standards.

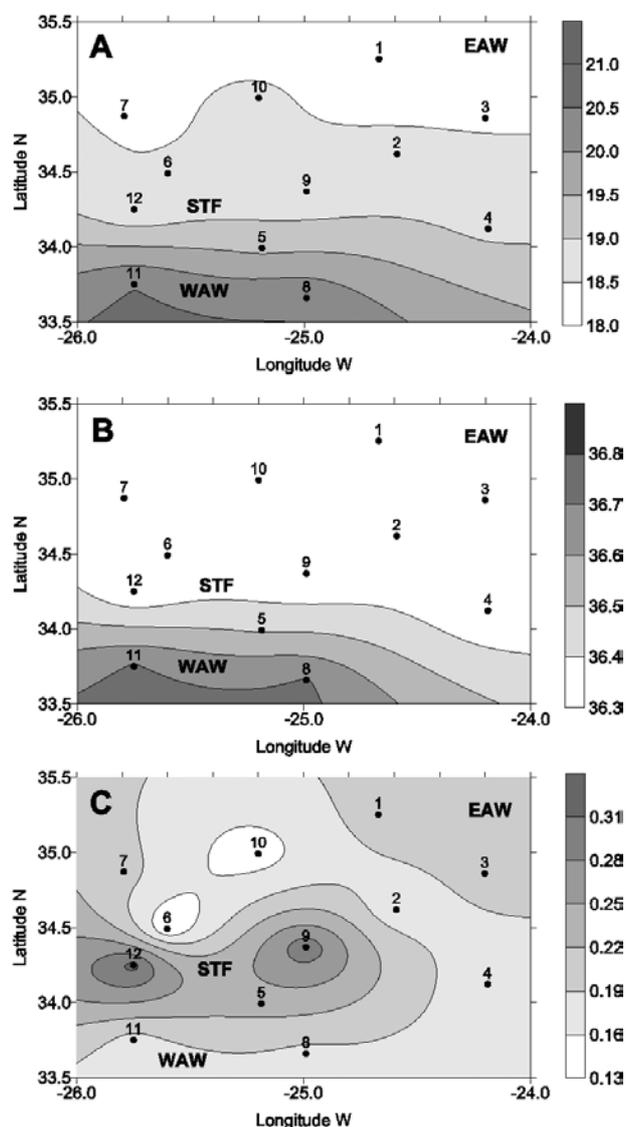


FIG. 2. – Distribution of (a) temperature ($^{\circ}\text{C}$), (b) salinity and (c) chlorophyll-a as integrated values in the upper 100 m (EAW: Eastern Atlantic Water; WAW: Western Atlantic Water). The location of the STF, stations positions and numbers are also indicated.

After removal of carbonates by HCl vapor in a desiccator (Hedges and Stern, 1984; Tanoue, 1985), particulate organic carbon and nitrogen were analysed by combustion using a CHNS-O EA 1108 Elemental Analyzer (Carlo Erba). Cyclohexanone was used as a standard.

RESULTS

Physical-chemical structure of the STF-AC system in June 1993

The subtropical front in June 1993 in the Azores-Madeira region was located between 33°N - 36°N

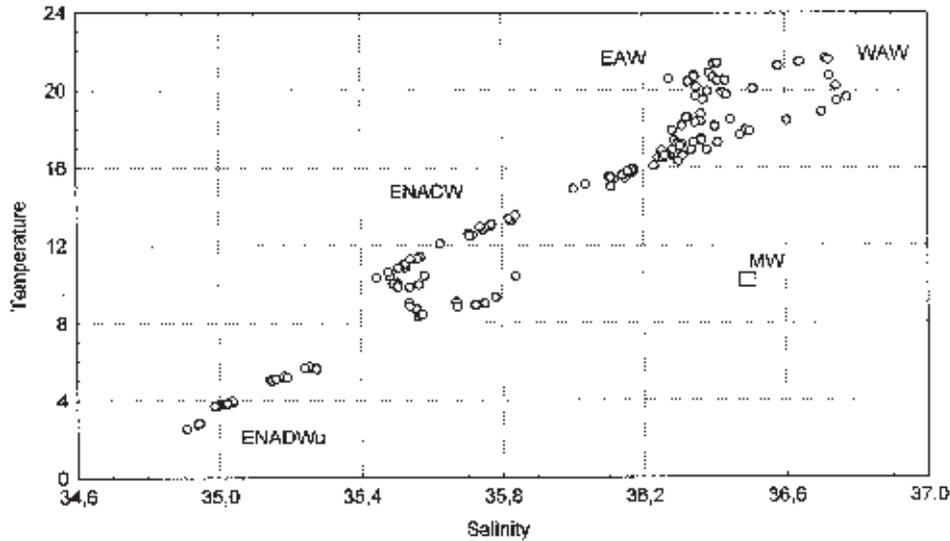


FIG. 3. – T-S diagram showing different water masses present in the area according to Tychensky (1998) (EAW: Eastern Atlantic Water; WAW: Western Atlantic Water; ENACW: Eastern North Atlantic Central Water; MW: Mediterranean Water, ENADWu: upper Eastern North Atlantic Deep Water).

and 24°W-26°W separating warmer more saline WAW from colder and fresher EAW (Tychensky, 1998). On the base of the temperature (T) and salinity (S) records four groups of stations were identified: sta. 8 and 11 showing the highest surface T and S values (0-100 m mean integrated values $>20.4^{\circ}\text{C}$ and >36.7) were defined as WAW stations; sta. 10, 2, 1, 3 showing the lowest surface T and S values (0-100 m mean integrated values $<18.7^{\circ}\text{C}$ and <36.4) were defined as EAW stations; sta. 9, 12 were identified as the frontal stations (STF) (Tychensky, 1998). Finally the remaining stations (sta. 4, 5, 6, 7) were identified as transitional between EAW and WAW (Fig. 2a, b). According to the fine-scale physical structure of the STF described by Tychensky (1998), the frontal line has been further highlighted

by the highest 0-100 m integrated chlorophyll-a concentrations as shown in Figure 2c.

Mediterranean Water (MW), which propagates to the south and southwest and crosses the Azores area, has been shown to cause relatively strong temperature and salinity (T-S) anomalies, leading to some dispersion in the T-S water mass diagram (Tychensky, 1998). Below the thermocline (0-100 m) the TS diagram as well as temperature and salinity profiles highlight the presence of a tongue of salt water (35.6 isohaline) arising from the influence of Mediterranean water at a depth of ~ 1000 m (Fig. 3). At greater depths, we found the upper part of North East Atlantic Deep Water (NEADWu), showing a range of temperatures and salinities values of 3°C - 6°C and 34.9-35.3 respectively.

TABLE 1. – Vertical distribution of chemical-physical parameters as mean values (\pm std) for WAW, STF and EAW stations respectively (reported are: temperature (T), salinity (S), nitrate (NO_3^-) and phosphate (PO_4^{3-})).

Depth (m) ↓	T ($^{\circ}\text{C}$)			S (‰)			NO_3^- ($\mu\text{mol l}^{-1}$)			PO_4^{3-} ($\mu\text{mol l}^{-1}$)		
	WAW	STF	EAW	WAW	STF	EAW	WAW	STF	EAW	WAW	STF	EAW
0	21.6 \pm 0.1	21.4 \pm 0.0	20.3 \pm 0.4	36.7 \pm 0.1	36.4 \pm 0.0	36.4 \pm 0.0	0.07 \pm 0.02	0.07 \pm 0.02	0.07 \pm 0.06	0.02 \pm 0.00	0.02 \pm 0.01	0.03 \pm 0.00
25	21.6 \pm 0.1	20.3 \pm 0.2	20.1 \pm 0.5	36.7 \pm 0.1	36.3 \pm 0.0	36.4 \pm 0.0	0.03 \pm 0.00	0.03 \pm 0.00	0.03 \pm 0.01	0.01 \pm 0.01	0.00 \pm 0.01	0.04 \pm 0.02
50	20.5 \pm 0.4	18.1 \pm 0.2	18.3 \pm 0.5	36.7 \pm 0.0	36.3 \pm 0.0	36.4 \pm 0.1	0.03 \pm 0.02	0.03 \pm 0.00	0.01 \pm 0.01	0.01 \pm 0.02	0.01 \pm 0.01	0.03 \pm 0.02
75	19.6 \pm 0.1	17.1 \pm 0.1	17.1 \pm 0.2	36.8 \pm 0.0	36.3 \pm 0.0	36.3 \pm 0.1	0.04 \pm 0.02	0.15 \pm 0.17	0.01 \pm 0.01	0.02 \pm 0.02	0.01 \pm 0.02	0.04 \pm 0.02
100	18.7 \pm 0.3	16.6 \pm 0.1	nd	36.7 \pm 0.1	36.3 \pm 0.0	nd	0.26 \pm 0.23	1.34 \pm 0.98	0.82 \pm 0.72	0.04 \pm 0.04	0.10 \pm 0.01	0.07 \pm 0.04
150	17.6 \pm 0.4	15.7 \pm 0.2	15.5 \pm 0.3	36.5 \pm 0.1	36.1 \pm 0.0	36.1 \pm 0.0	2.60 \pm 0.77	2.86 \pm 1.36	2.50 \pm 0.72	0.12 \pm 0.03	0.17 \pm 0.06	0.18 \pm 0.03
300	15.4 \pm 0.7	13.3 \pm 0.3	12.9 \pm 0.3	36.1 \pm 0.1	35.8 \pm 0.0	35.8 \pm 0.0	5.63 \pm 1.18	7.33 \pm 0.41	7.56 \pm 0.52	0.35 \pm 0.09	0.51 \pm 0.03	0.57 \pm 0.04
500	12.6 \pm 0.1	11.2 \pm 0.2	11.0 \pm 0.3	35.7 \pm 0.0	35.5 \pm 0.0	35.5 \pm 0.0	14.15 \pm 0.32	15.54 \pm 0.23	15.51 \pm 0.31	0.59 \pm 0.05	0.82 \pm 0.04	0.87 \pm 0.08
700	10.5 \pm 0.2	9.9 \pm 0.0	10.1 \pm 0.3	35.5 \pm 0.0	35.5 \pm 0.0	35.6 \pm 0.2	16.07 \pm 0.19	16.27 \pm 0.42	16.41 \pm 0.16	0.92 \pm 0.02	0.97 \pm 0.05	1.01 \pm 0.05
1000	9.0 \pm 0.1	8.4 \pm 0.0	9.0 \pm 0.2	35.5 \pm 0.0	35.6 \pm 0.0	35.7 \pm 0.0	16.66 \pm nd	16.55 \pm 0.03	16.49 \pm 0.07	0.91 \pm 0.23	1.04 \pm 0.01	1.04 \pm 0.00
1500	5.7 \pm 0.1	5.1 \pm 0.1	5.2 \pm 0.1	35.2 \pm 0.0	35.2 \pm 0.0	35.2 \pm 0.0	16.49 \pm 0.06	16.49 \pm 0.03	16.53 \pm 0.04	1.06 \pm 0.01	1.07 \pm 0.01	1.09 \pm 0.02
2000	2.8 \pm 0.0	3.3 \pm 0.8	3.6 \pm 0.5	34.9 \pm 0.0	35.0 \pm 0.1	35.0 \pm 0.0	17.16 \pm nd	16.80 \pm 0.42	16.51 \pm 0.55	1.01 \pm 0.37	1.13 \pm 0.12	1.20 \pm 0.16

nd=not determined

TABLE 2. – Vertical distribution of biochemical parameters as mean values (\pm std) for WAW, STF and EAW stations respectively (reported are: particulate organic carbon (POC), particulate organic nitrogen (PON), particulate proteins (PPRT), particulate carbohydrates (PCHO), chlorophyll-a (CHL-a) and phaeopigments (PHAEO)).

Depth (m)	POC ($\mu\text{gC l}^{-1}$)			PON ($\mu\text{gN l}^{-1}$)			PPRT ($\mu\text{g l}^{-1}$)		
	WAW	STF	EAW	WAW	STF	EAW	WAW	STF	EAW
0	35.9 \pm 12.9	45.9 \pm 2.2	41.0 \pm 4.1	5.0 \pm 0.0	6.1 \pm 1.2	5.3 \pm 0.8	36.9 \pm 3.9	38.7 \pm 3.9	37.2 \pm 7.9
25	42.4 \pm 5.1	50.4 \pm 1.1	42.9 \pm 2.6	5.2 \pm 0.4	6.1 \pm 0.6	6.0 \pm 1.0	38.2 \pm 0.5	38.6 \pm 7.8	40.6 \pm 8.4
50	41.1 \pm 3.9	53.9 \pm 12.6	49.0 \pm 8.2	5.2 \pm 0.2	6.9 \pm 1.1	6.2 \pm 1.1	35.4 \pm 1.5	43.2 \pm 1.7	38.5 \pm 4.4
75	36.7 \pm 3.1	55.6 \pm 3.2	45.7 \pm 8.1	5.7 \pm 1.1	8.3 \pm 0.7	6.3 \pm 1.8	31.1 \pm 0.2	51.9 \pm 9.5	46.2 \pm 13.2
100	44.6 \pm 0.9	33.7 \pm 2.0	43.3 \pm 8.4	6.4 \pm 0.3	4.4 \pm 0.3	5.8 \pm 2.0	39.0 \pm 4.6	30.2 \pm 2.8	39.0 \pm 10.1
150	nd	25.5 \pm 7.6	25.9 \pm 5.9	nd	2.6 \pm 0.5	2.7 \pm 1.2	33.7 \pm 8.2	20.2 \pm 2.6	23.2 \pm 2.6
300	21.1 \pm 5.8	18.7 \pm 4.8	24.8 \pm 8.2	2.8 \pm 1.0	2.5 \pm 0.7	3.2 \pm 1.6	25.4 \pm 0.5	21.0 \pm 4.1	21.9 \pm 2.8
500	23.6 \pm 9.9	15.9 \pm 3.9	20.7 \pm 4.4	2.9 \pm 1.6	2.2 \pm 0.6	3.0 \pm 1.3	20.2 \pm 4.9	20.6 \pm 6.0	17.7 \pm 6.7
700	14.3 \pm 4.7	18.5 \pm 5.9	17.6 \pm 3.3	1.9 \pm 0.0	2.4 \pm 0.1	2.3 \pm 1.1	19.9 \pm 3.3	18.9 \pm 4.5	29.4 \pm 11.0
1000	18.3 \pm 2.1	21.5 \pm 5.7	17.5 \pm 6.7	1.9 \pm 0.1	2.7 \pm 0.2	2.1 \pm 1.1	21.6 \pm 5.2	24.6 \pm 1.2	16.2 \pm 6.9
1500	20.5 \pm 4.0	20.8 \pm 3.9	20.5 \pm 8.4	2.4 \pm 0.5	2.4 \pm 0.2	2.5 \pm 1.3	28.5 \pm 17.7	28.6 \pm 1.1	25.3 \pm 11.2
2000	22.1 \pm 5.0	28.0 \pm 7.6	20.1 \pm 11.5	2.1 \pm 0.2	3.8 \pm 2.1	2.2 \pm 1.5	28.9 \pm 7.2	20.2 \pm 0.4	17.0 \pm 3.1

	PCHO ($\mu\text{g l}^{-1}$)			CHL-a ($\mu\text{g l}^{-1}$)			PHAEO ($\mu\text{g l}^{-1}$)		
	WAW	STF	EAW	WAW	STF	EAW	WAW	STF	EAW
0	22.2 \pm nd	27.3 \pm nd	26.0 \pm 17.5	0.1 \pm 0.0	0.1 \pm 0.0	0.1 \pm 0.0	0.0 \pm 0.0	0.0 \pm 0.0	0.0 \pm 0.0
25	17.6 \pm nd	28.8 \pm nd	20.2 \pm 4.3	0.1 \pm 0.0	0.1 \pm 0.0	0.1 \pm 0.0	0.0 \pm 0.0	0.0 \pm 0.0	0.0 \pm 0.0
50	18.7 \pm nd	24.4 \pm nd	27.6 \pm 3.1	0.1 \pm 0.0	0.2 \pm 0.1	0.1 \pm 0.0	0.0 \pm 0.0	0.1 \pm 0.0	0.0 \pm 0.0
75	17.3 \pm nd	18.6 \pm nd	17.5 \pm 3.8	0.2 \pm 0.0	0.8 \pm 0.1	0.3 \pm 0.1	0.1 \pm 0.0	0.3 \pm 0.0	0.2 \pm 0.1
100	12.5 \pm nd	13.7 \pm nd	17.0 \pm 1.6	0.5 \pm 0.0	0.2 \pm 0.1	0.4 \pm 0.1	0.2 \pm 0.1	0.2 \pm 0.0	0.3 \pm 0.0
150	14.4 \pm nd	5.2 \pm nd	11.5 \pm 3.0	0.1 \pm 0.1	0.0 \pm 0.0	0.1 \pm 0.1	0.1 \pm 0.1	0.1 \pm 0.0	0.1 \pm 0.0
300	11.0 \pm nd	7.0 \pm nd	10.5 \pm 1.9	nd	nd	nd	nd	nd	nd
500	11.1 \pm nd	4.8 \pm nd	6.0 \pm 3.5	nd	nd	nd	nd	nd	nd
700	14.7 \pm nd	7.0 \pm nd	6.0 \pm 1.6	nd	nd	nd	nd	nd	nd
1000	8.6 \pm nd	4.0 \pm nd	9.1 \pm 2.7	nd	nd	nd	nd	nd	nd
1500	15.1 \pm nd	9.4 \pm nd	4.0 \pm 4.5	nd	nd	nd	nd	nd	nd
2000	11.3 \pm nd	3.7 \pm nd	4.8 \pm 0.97	nd	nd	nd	nd	nd	nd

Data on physical and chemical parameters for the different water masses are summarized in Table 1 (as previously described selected stations used to average the data were: sta. 8 and 11 for Western Atlantic Water (WAW), sta.10, 2, 1, 3 for Eastern Atlantic Water (EAW) and sta. 9, 12 for the frontal line section (STF)).

Phosphate and nitrate concentrations were almost depleted in the surface layer (upper 100 m) and were close to the detection limit ($\text{NO}_3^- < 0.15 \mu\text{mol l}^{-1}$; $\text{PO}_4^{3-} < 0.06 \mu\text{mol l}^{-1}$). In contrast, differences in nutrient concentrations became evident at ~ 500 m with lower values ranging from 13.9-14.4 $\mu\text{mol l}^{-1}$ for nitrates and 0.5-0.7 $\mu\text{mol l}^{-1}$ for phosphates and higher values ranging from 15-15.7 $\mu\text{mol l}^{-1}$ for nitrates and 0.8-1 $\mu\text{mol l}^{-1}$ for phosphates in the WAW and EAW stations, respectively.

Nutrient concentrations increased with increasing depth up to mean values of 16.6 $\mu\text{mol l}^{-1}$ for nitrates and 1.0 $\mu\text{mol l}^{-1}$ for phosphates detected at a depth of 1000 m. From 1000 to 2000 m depth only a slight increase has been observed for both nitrate and phosphate concentrations.

Biochemical composition of POM in the Azores-Madeira region

Elemental and biochemical composition of particulate organic matter (POM) was investigated for POC, PON, proteins, carbohydrates and phytopigments in the Azores-Madeira region down to a depth of 2000 m; data on the vertical distribution of biochemical variables for the different water masses are summarized in Table 2. POC and PON vertical profiles on a section crossing the frontal line showed highest surface values at frontal stations (Fig. 4). POC and PON concentrations ranged, in the surface layer, between 23.3-64.5 $\mu\text{gC l}^{-1}$ and 2.9-9.1 $\mu\text{gN l}^{-1}$, respectively, and decreased with depth to mean values of 18.5 $\mu\text{gC l}^{-1}$ and 2.3 $\mu\text{gN l}^{-1}$ at 500 m depth and 16.7 $\mu\text{gC l}^{-1}$ and 1.9 $\mu\text{gN l}^{-1}$ at 1000 m depth. No further changes were detected for POC and PON concentrations at greater depths.

A DCM was observed at ~ 75 m depth at stations 9 and 12 located on the frontal boundary, and ~ 100 m depth for the remaining sampling stations (Fig. 5). Chlorophyll-a concentrations in the surface water did not exceed 0.4 $\mu\text{g l}^{-1}$ except at frontal stations 9

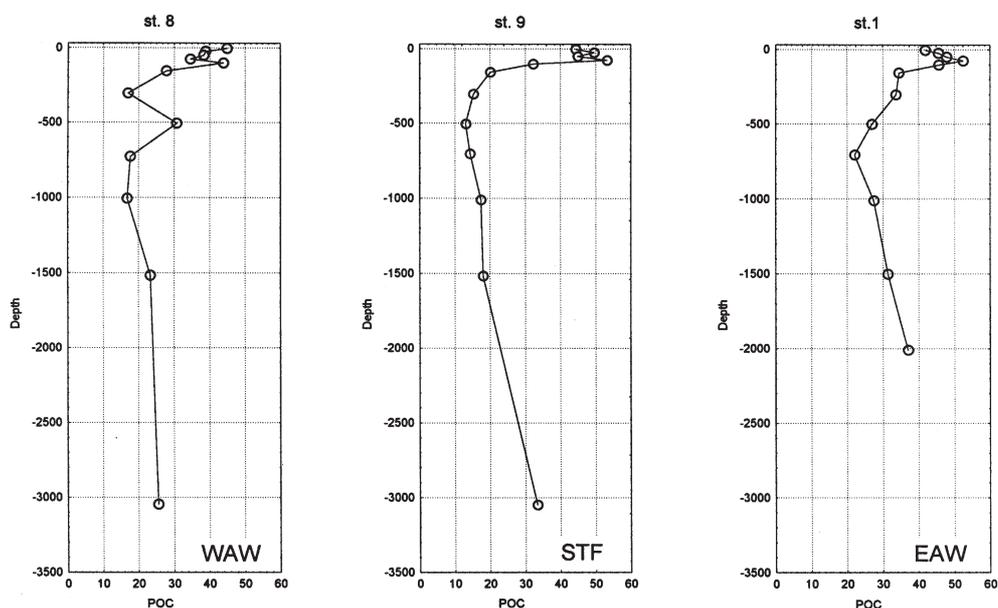


FIG. 4. – Vertical distribution of POC in $\mu\text{gC l}^{-1}$ for st. 8 (WAW), st.9 (STF) and st.1 (EAW).

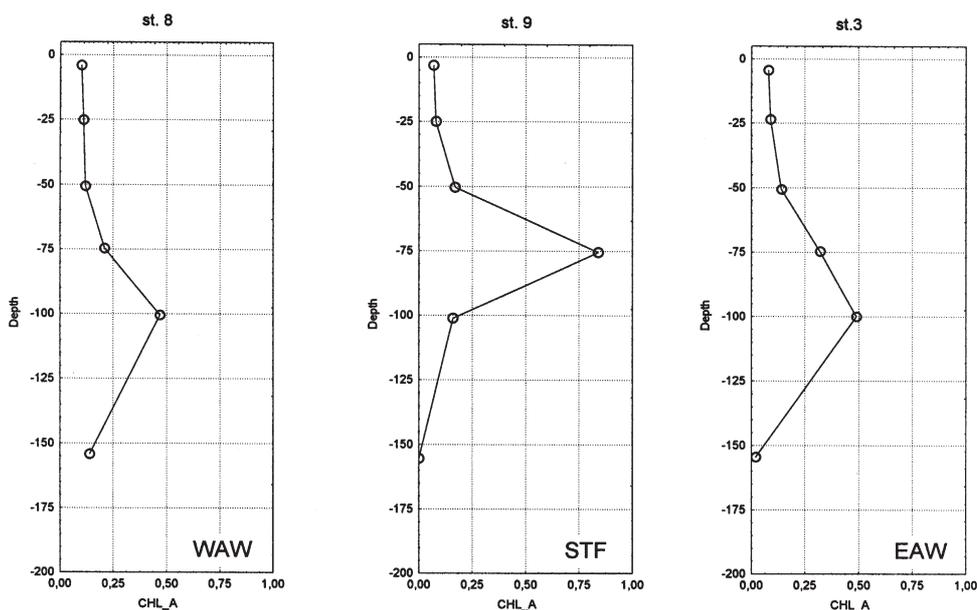


FIG. 5. – Vertical distribution of chlorophyll-a in $\mu\text{g l}^{-1}$ for st. 8 (WAW), st.9 (STF) and st.3 (EAW).

and 12 were chlorophyll-a reached $0.8 \mu\text{g l}^{-1}$. Phaeopigment values were generally lower than those observed for chlorophyll-a in the surface layer, ranging from 0 (below detection for spectrophotometric analysis) to $0.2 \mu\text{g l}^{-1}$.

Particulate proteins and carbohydrates were also very low and were on average $40 \mu\text{g l}^{-1}$ and $22.2 \mu\text{g l}^{-1}$ in the surface layer, respectively. As observed for POC and PON, the values decreased with depth, reaching mean concentrations of 19.5

$\mu\text{g l}^{-1}$ for proteins and $5.7 \mu\text{g l}^{-1}$ for carbohydrates at a depth of 500 m. A further decrease in protein concentrations occurred at a depth of 1000 m, with mean values reaching $18 \mu\text{g l}^{-1}$, while carbohydrates increased slightly up to mean concentrations of $7.0 \mu\text{g l}^{-1}$.

At greater depths, an increase in protein concentrations also occurred with mean values reaching $25.4 \mu\text{g l}^{-1}$ and $22.4 \mu\text{g l}^{-1}$ at a depth of 1500 m and 2000 m, respectively.

DISCUSSION

In the Canary basin the very low values of POC, PON, nutrients and chlorophyll-a concentrations in the surface layer were in agreement with other studies carried out in the North East Atlantic (Ríos *et al.*, 1995; Pérez *et al.*, 1998; Castro *et al.*, 1998; Hall *et al.*, 2000), and were comparable with values found in other areas of the open ocean such as the North Pacific gyre (Sharp *et al.*, 1980; Eppley *et al.*, 1988), the deep southern Pacific (Fabiano *et al.*, 2000; Povero *et al.*, 2000) and several oligotrophic areas in the Mediterranean Sea (Bethoux *et al.*, 1998; Danovaro *et al.*, 2000). At 1000 m depth, inorganic nutrients showed higher average values than found in deep layer outflows across the Straits of Gibraltar (Bethoux *et al.*, 1998) and in the Tyrrhenian Sea (Povero *et al.*, 1990); in contrast, POC and PON concentrations were lower in comparison to Mediterranean deep water (Tselepidis *et al.*, 2000) and seemed in agreement with the low productivity of this area (Fernandez *et al.*, 1996).

The C:N ratio of the suspended matter in the euphotic zone was higher (mean C:N ratio 7.9) than some values obtained in the equatorial Atlantic (C:N 6.1; Herbland and le Bouteiller, 1983) and in several other oceanic regions (Copin-Montegut and Copin Montegut, 1983), suggesting that the particulate matter in our study region was mostly of detrital origin. The particulate material below the euphotic zone in our region had a C:N ratio of 7.9-9.4 in the euphotic zone indicating preferential N removal.

All POC:Chl-a ratios were very high (mean of all surface layers = 363.7) with values double those observed in other oceanic regions such as the equatorial Pacific (Pena *et al.*, 1991), suggesting that the local autotrophic component accounts for a low fraction of POM. In contrast, low values of the

POC:Chl-a ratios has been found in the DCM. The Chl-a:PPRT ratio, which is an indicator of autotrophic/total biomass (Dortch and Packard, 1989) is also highest in the DCM, indicating high autotrophic biomass (refer to the material and methods section for an explanation of the problems arising from the use of different types of filters).

The PPRT:PCHO ratio is employed to characterise the POM biochemical fraction and, to a certain extent, to assess its "age" (Fabiano *et al.*, 1993). The PPRT:PCHO ratio averaged 1.9 in the surface layer with the highest values (up to 3.4) observed at frontal stations in the DCM. The dominance of the proteins as suggested by high PPRT:PCHO ratios are characteristics of highly productive areas such as lagoons (Pusceddu *et al.*, 1996) and estuaries (Navarro *et al.*, 1993), but have also been reported during phytoplankton blooms in oligotrophic areas, such as the Ligurian Sea (Fabiano *et al.*, 1984). However, while the concentrations of chlorophyll-a and particulate proteins decreased with increasing depth in response to grazing activity and decomposition processes, the PPRT:PCHO ratio remained quite high and is sometimes higher in deep water than at the surface. The high PPRT:PCHO ratio found in the deep water, below the thermocline, is in agreement with the "protein enrichment" observed by Fabiano *et al.* (2001) in fresh detritus, mainly caused by the bacterial colonization of particles due to the low values (about 4) of the bacterial C:N ratio (Lee and Fuhrman, 1987). Thus, the persistence of the protein dominance in POM with increasing depth in the Canary Basin may be related to the marked oligotrophy of these waters, where microbial communities may achieve a high importance in the biochemical composition of POM (Cho and Azam, 1988).

During June 1993, the DCM was well established and conversely to what was observed by

TABLE 3. – Mixed layer integrated values (0-100 m) of selected biological variables for WAW, STF and EAW stations.

Variables	WAW (sta 8,11)	STF (sta 9,12)	EAW (sta 10,2,1,3)	one-way ANOVA <i>p</i> -level
Integrated POC 0-100m ($\mu\text{gC l}^{-1}$)	40.09	49.9	44.9	0.07
Integrated PON 0-100m ($\mu\text{gN l}^{-1}$)	5.5	6.6	6.0	0.32
Integrated particulate proteins 0-100m ($\mu\text{g l}^{-1}$)	35.7	42.0	40.9	0.34
Integrated particulate carbohydrates 0-100m ($\mu\text{g l}^{-1}$)	17.7	23.1	21.7	0.55
Integrated POC/Chl-a ratio 0-100m	297.4	346.7	447.1	nd
Depth of the DCM (m)	100	75	100	nd
Chlorophyll-a ($\mu\text{g l}^{-1}$) at the DCM	0.5	0.8	0.4	nd
POC/Chl-a ratio at the DCM	174.8	154.1	172.5	nd
Chl-a/PPRT ratio at the DCM	0.013	0.015	0.010	nd

nd = not detected

Fasham *et al.* (1985) it appeared on average 20 m shallower (DCM depth=75 m) and of greater magnitude (Chl-*a*=0.8 $\mu\text{g l}^{-1}$) at the frontal stations, while no significant differences were evident in its magnitude and depth between WAW and EAW (Fig. 5). A difference has been highlighted in the vertical distribution of POC and PON with higher concentration detected at stations 2, 10, 1 belonging to EAW (Table 2, Fig. 4). In contrast, the lowest values of POC and PON as well as particulate proteins and carbohydrates were found in the WAW.

Statistical analysis was carried out to further define the differences detected in the quantity and quality of POM between EAW and WAW. The regression between POC versus PON was used as a first attempt to investigate such a difference. POC and PON concentrations showed high correlation if calculated for all data but, in agreement with Copin-Montegut (1983) in several oceanic areas no significant changes (T-statistics, $p>0.05$) were evident in the slopes and intercepts of the regression lines for the different water types.

On the contrary, the study of mean integrated values of selected biochemical variables in the upper 100 m highlighted the difference occurring in WAW, EAW as well as frontal stations on the basis of particulate matter composition (Table 3). WAW showed the smallest integrated concentrations of particulate organic carbon, particulate organic nitrogen, particulate proteins and particulate carbohydrates; by contrast frontal stations showed the highest concentrations while EAW stations had intermediate values. All these results coupled with the highest POC:Chl-*a* ratio found in EAW suggest a possible delay occurring in the production cycle between the two water masses. Alternatively, the WAW is a more stratified and oligotrophic body of water than is EAW, and it always has lower biomass and nutrients than the more productive EAW. In this case, there may not be a temporal offset but, rather, an annually averaged difference as well.

In conclusion, the differences in quantity and quality of particulate material found between water masses suggest that the analysis of POM can be of great help in determining the state of biological processes occurring in this area; furthermore in agreement with previous investigations (Fernandez and Pingree, 1996) the biological signature associated with the STF-AC system supports the conclusion that carbon fixation within the frontal structure might be of significance for regional carbon budgets of the subtropical northeast Atlantic.

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