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Dissolved organic carbon distributions in the Bransfield and Gerlache Straits, Antarctica

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Abstract

During FRUELA'95 cruise, seawater samples were collected at the Bransfield and Gerlache Straits for the analysis of dissolved organic carbon (DOC) profiles throughout the water column. An excess of DOC probably derived from phytogenic material was observed in the upper mixed layer (UML; average: $+22\pm13\,\mu mol\ C\,l^{-1}$), compared to the constant concentration of refractory DOC below 400 m ($44\pm4\,\mu mol\ C\,l^{-1}$). The average excess DOC concentration was higher than the particulate organic carbon concentration indicating the major contribution of DOC to carbon export in this area. However, large spatial variability of DOC in the upper mixed layer (52–$102\,\mu mol\ C\,l^{-1}$) was observed: excess DOC contributed from 15% to 57% to the actual DOC concentration. Maximum average DOC concentrations in the UML were recorded in the Gerlache Strait ($71\,\mu mol\ C\,l^{-1}$) and in the Gerlache–Bransfield confluence ($80\,\mu mol\ C\,l^{-1}$), whereas minimum values were recorded in the Bransfield Strait ($61\,\mu mol\ C\,l^{-1}$).

Several shelf and slope stations showed a slight increase of DOC (5–$10\,\mu mol\ C\,l^{-1}$) in the deep layer which might be related to organic matter release from the underlying sediments. Considering the net DOC release from phytoplankton, the low bacterial biomass and the reduced vertical DOC export, the DOC excess could build up in about 6 days for most of the sampling stations. The probable fate of the DOC excess is the eastwards horizontal transport by the Bransfield Current out of the study area. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

A dissolved organic matter (DOM) excess in surface ocean waters compared to deep waters is a commonly observed worldwide trend (Thingstad et al. (1997) and references therein). The contribution of this amount of DOM to the export of primary production is a subject of continued discussion (e.g., Legendre and Le Févre, 1995; Hansell and Carlson, 1998a). The excess surface DOM can be: (1) consumed by heterotrophic bacteria; (2) exported downwards by turbulent diffusion or during deep winter convection (Copin-Montégut and Avril, 1993; Carlson et al., 1994); or (3) transported out of the production area by horizontal circulation (Legendre and Le Févre, 1995; Hansell and Waterhouse, 1997). This excess DOM has been hypothesized to be composed of semi-labile and labile material with recycling time of days to months. However, deep DOC is composed mostly of refractory material with recycling time of $\sim 10^{1-3}$ years (Copin-Montégut

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and Avril, 1993; Carlson and Ducklow, 1995). In agreement with the most recently studies, refractory DOC is not constant for all deep waters around the world; deep DOC concentrations decrease about 14 μM C from the northern North Atlantic Ocean to the northern North Pacific Ocean (Hansell and Carlson, 1998b).

There exists a wide range of measured DOC concentrations in the Southern Ocean: from 6 to 1000 μmol C l^{-1} (Dafner (1992); Dafner and Selin (1995); Karl et al. (1996) and references therein). More realistic values between 40 and 100 μmol C l^{-1} were measured in the Weddell Sea (Skoog and Wedborg, 1994; Wedborg et al., 1998), from 38 to 60 μmol C l^{-1} along 6°W between 47° and 60°S (Kähler et al., 1997), from 33 to 105 μmol C l^{-1} along 62°E between 49° and 66°S (Wiebinga and De Baar, 1998), from 40 to 72 μmol C l^{-1} in the Ross Sea (Carlson et al., 1998) and from 40 to 70 μmol C l^{-1} along 170°E and 170°W between 50° and 67°S (Doval and Hansell, 2000). The wider ranges in the earlier papers were related to analytical difficulties or special marine environments (Dawson et al., 1985).

Antarctic waters range from oligotrophic regions to productive coastal embayments (Karl, 1991). The Bransfield and Gerlache Straits, located in the coastal zone of the Antarctic Peninsula, are characterized by a complex circulation pattern involving waters from the surrounding Weddell Sea, Bellingshausen Sea and Drake Passage (Niiler et al., 1991). This coastal zone shows a wide spatial and temporal range of phytoplankton production (Priddle et al., 1986; Holm-Hansen and Mitchell, 1991; Karl et al., 1991a).

A mesoscale study in this area was carried out during the RACER program (November 1986–March 1987; Karl, 1991; Huntley et al., 1991) with the main objective of studying the physical and biological processes causing the high productivity observed in coastal waters of the Antarctic Peninsula (Huntley et al., 1991). Despite DOC not being measured, outputs from the RACER carbon model suggested production of a large amount of labile DOC (Karl et al., 1991a). Aristegui and Montero (1995) and Aristegui et al. (1996) suggested large exudation of DOC in the same area to explain their measurements of community respiration and the discrepancy between primary production measured by ^{14}C and O_2 methods.

Another three main conclusions from the RACER program will be specially considered in this paper: (1) the upper mixed layer (UML) depth controlled the development of the spring bloom (Mitchell and Holm-Hansen, 1991); (2) a microbial food web dominated by phytoplankton was characteristic during the initial phase of the bloom (Karl et al., 1991b); and (3) the Bransfield current could be important for transporting and redistributing biogenic material from eutrophic regions of the northern Gerlache Strait to the Drake Passage in a period of 15–30 days (Niiler et al., 1991).

The main objective of the FRUELA project was the study of carbon fluxes in an area of elevated productivity in the Antarctic Ocean: the Gerlache and Bransfield Straits. The present work deals with the spatial and vertical variability of DOC. The origin and fate of the observed excess surface DOC were studied as well as the relationship of DOC with other water masses tracers.

2. Material and methods

The results presented here correspond to a grid of four transects in the western basin of the Bransfield Strait and one transect along the Gerlache Strait, occupied from 10 to 18 December 1995 during the FRUELA'95 expedition, aboard the Antarctic R/V '*Hespérides*'. Sample locations are shown in Fig. 1.

Salinity and temperature were recorded by means of a conductivity-temperature-depth (CTD) Mark IIIC probe. Water samples were collected with a General Oceanic rosette sampler (24 10 l Niskin bottles) attached to the CTD system.

Seawater samples for DOC analysis were collected at 27 stations spaced 9–18 km apart at the surface, fluorescence maximum, 100 m bottom and three more depths depending on the bathymetry. Samples were collected with 100 ml polyethylene syringes with teflon plunger tips and filtered by hand through Whatman Puradisc GF/F

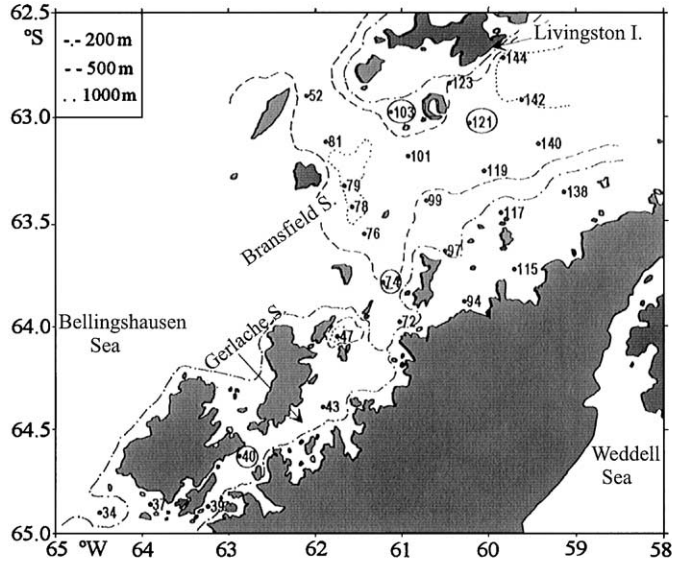

Fig. 1. Map of the DOC sampling grid consisting of four transects in the western basin of the Bransfield Strait and one transect along the Gerlache Strait during the FRUELA'95 cruise. Open circles marked selected stations presented in Fig. 3.

disposable filter devices (0.7 μm pore size) on polypropylene housing. The filtrate was drawn eventually into 50 ml polyethylene containers. The filtering system and the containers used for DOC had been previously soaked in 0.1 N HCl, and rinsed with Milli-Q water. In addition, the containers were rinsed three times with 50 ml of sample. Samples were immediately stored at $-70^{\circ}C$ until analysis in the base laboratory, eight months later. This storage technique has demonstrated no artifactual results on the micromolar scale (Hansell and Carlson, 1998b).

DOC determination was performed by high-temperature catalytic oxidation (HTCO) with a commercial Shimadzu TOC-5000. The combustion quartz tube was filled with 0.5% Pt on Al_2O_3 catalyst. Three to five replicate injections of 200 μl were performed per sample. The concentration of DOC was determined by subtracting the average peak area from the instrument blank area and dividing by the slope of the standard curve. The instrument blank is the system blank plus the filtration blank. The system blank was determined by subtracting the DOC in UV-Milli-Q from the total blank. Measurements made with the high-sensitivity catalyst (Pt on silica wool) produced values $<2\,\mu mol\ C\,l^{-1}$ for fresh UV-Milli-Q water. The filtration blank (determined by filtering UV-Milli-Q water through the filtration system) was $<2\,\mu mol\ C\,l^{-1}$. Before sample analyses, the catalyst was washed by injecting UV-Milli-Q for at least 12 h, until the system blank was low and stable. The system blank was $<8\,\mu mol\ C\,l^{-1}$. The device was standardized with potassium hydrogen phthalate (KHP). The coefficient of variation (CV) of the peak area for 3–5 replicate analyses of each sample was $\sim 1\%$. The accuracy of our HTCO system has been tested within the international intercalibration exercise conducted by J. Sharp (University of Delaware) with very satisfactory results (within $\pm 10\%$; J. Sharp, pers. comm.).

Seawater samples for particulate organic matter (POM), chlorophyll *a* (chl *a*), nutrients and oxygen were also collected. Sampling depths for POM were the same as DOC analysis; every 10 m between the surface and 100 m depth for chl *a*, and surface, every 20 m between 20 and 100, 200, 250 m, every 100 m between 300 and 600, 800, 1000 m, and every 300 or 500 m between 1000 m and bottom (depending on bathymetry) for nutrients.

One liter of sample was filtered through an oilless vacuum filtration system. Particulate organic carbon (POC) and nitrogen (PON) were collected on Whatman GF/F filters, which were dried on silica gel and frozen to $-70°C$ until analysis in the base laboratory. Measurements were carried out with a Perkin Elmer 2400 CHN analyzer. Combustion to CO_2 and NO_x was performed at 900°C and reduction of NO_x to N_2 at 640°C. Chl *a* was determined fluorometrically, with a Turner Designs 10000R fluorometer after 90% acetone extraction (Yentsch and Menzel, 1963). Samples for nutrients analyses were collected on 100 ml polyethylene syringes and filtered by hand through Whatman Puradisc 25 disposable filters (polypropylene filter media: 0.45 μm pore size) on polypropylene housing. The filtrate was drawn into 50 ml polyethylene containers and analyzed immediately using standard segmented flow analysis procedures (Castro et al., 2002).

3. Results and discussion

3.1. Hydrographic conditions

According to García et al. (2002) silicate is a very good discriminator of water masses in the FRUELA area. To study the spatial variability of DOC, chl *a* and POC in relation to water masses, we have displayed the silicate distributions at two reference levels: the upper mixed layer (UML) and 200 m (Fig. 2b and c).

Fig. 2a shows the UML depth (Z_{UML}), calculated following Castro et al. (2002). Shallower UMLs ($\leqslant 20$ m) were found in the southeastern corner of the Bransfield Strait and in the Gerlache Strait with the exception of stn 40. Stratification in the northeastern part of the Gerlache Strait was due to the presence of a warm ($T > -1.0°C$) and diluted ($S < 33.5$) water layer. In the southeastern part of the Gerlache Strait and in the southeastern sector of the Bransfield Strait, melting ice favored the strong water-column stratification (García et al., 2002).

The horizontal distribution of silicate integrated over the UML (Fig. 2b) discerns between the Transition Zonal Water with Bellingshausen influence (TBW) and the Transitional Zonal Water dominated by Weddell Sea influence (TWW) in the Bransfield Strait (García et al., 2002). The silicate isopleth of 79 μmol kg^{-1} coincides with the 34.1 isohaline and can be considered the limit between TBW ($SiO_2 \leqslant 79$ μmol kg^{-1}) and TWW. The northeast advection of surface water from the Gerlache Strait is discerned by the highest silicate levels in the area ($\geqslant 84$ μmol kg^{-1}). At 200 m depth (Fig. 2c), the Bransfield Front separates the intrusion of lower circumpolar deep water (LCDW) with high silicate concentrations (>85 μmol kg^{-1}) from TWW with lower levels (García et al., 2002). In the Gerlache Strait, the high silicate levels (>94 μmol kg^{-1}) correspond to LCDW warmer and saltier ($\theta = 0.7 \pm 0.1°C$, $S = 34.50 \pm 0.01$) than LCDW in the northwestern part of the Bransfield Strait ($\theta = 0.07 \pm 0.3°C$; $S = 34.41 \pm 0.06$; $SiO_2 = 87 \pm 4$ μmol kg^{-1}). In the Bransfield–Gerlache confluence lower silicate levels correspond to the TWW. Below 400 m, TWW fills the entire Bransfield Strait with a mean silicate concentration of 86 ± 3 μmol kg^{-1} and salinity of 34.56 ± 0.02.

3.2. Vertical DOC profiles

The average DOC profile for the study area (mean ± SD) decreased from 66 ± 13 μmol C l^{-1} in the UML to 44 ± 4 μmol C l^{-1} in deep waters (>400 m). Selected DOC profiles at stn 40 in the Gerlache Strait, stn 74 in the Gerlache–Bransfield confluence, stn 103 in the Bransfield Strait, and stn 121 at the Bransfield Front (Fig. 3) illustrate the observed vertical variability.

The correlation of DOC with density was low ($r^2 < 0.1$) in the whole water column indicating the low control of hidrography on the distribution of DOC. Stns 74 and 121 showed a DOC maximum at the base of UML (i.e. in the bottom layer of UML) as well as most of the sampling stations (70%). Despite similar chl *a* levels, DOC concentrations were very different between these stations. Concentration at the DOC maximum was higher in the Gerlache–Bransfield confluence (stn 74; 120 μmol C l^{-1}) than in the Bransfield Front (stn 121; 75 μmol C l^{-1}). The chl *a* maximum at these stations (>4 mg m^{-3}) was apparently shallower

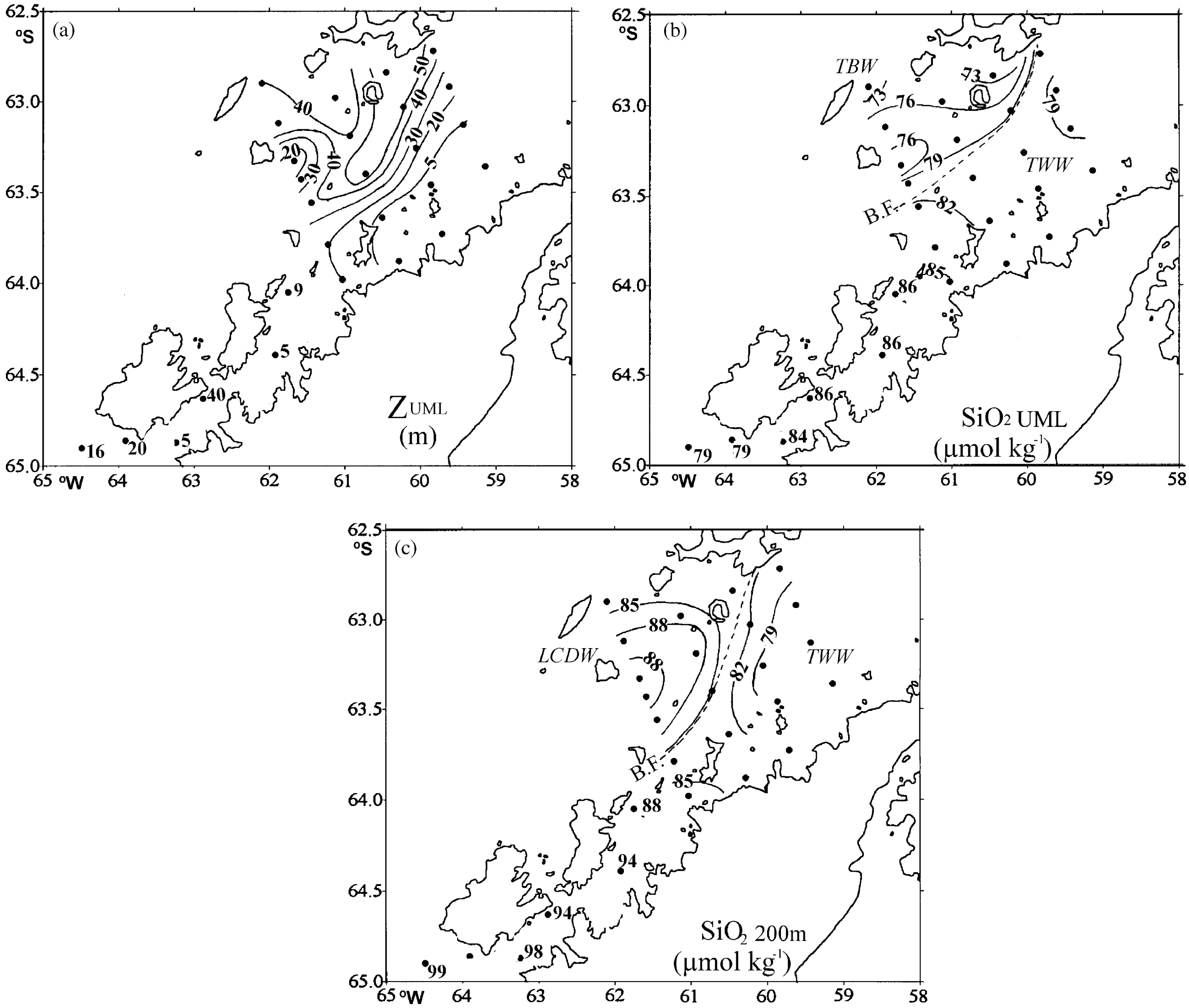

Fig. 2. Spatial distribution of (a) upper mixed-layer depth (Z_{UML}, *m*), (b) averaged depth-integrated silicate (µmol kg^{-1}) in the upper mixed layer, and (c) silicate at 200 m depth (µmol kg^{-1}). TBW: Transition Zonal Water with Bellingshausen Sea influence; TWW: Transition Zonal Water with Weddell Sea influence; LCDW: Lower circumpolar deep water; BF: Bransfield Front.

than the DOC maximum, in agreement with the distributions of TOC found by Wedborg et al. (1998) at productive stations in the Weddell Sea.

Conversely, at other stations the DOC maximum can be located within the UML. This is the case of stn 40, where the DOC maximum was at 20 m coinciding with the subsurface chl *a* maximum ($\sim$4 mg m^{-3}). This station in the Gerlache Strait showed the highest DOC values in the study area, although the average DOC value in the upper mixed layer (102 µmol C l^{-1}; Fig. 4c) was similar to that obtained in the Gerlache–Bransfield confluence (stn 72 : 99 µmol C l^{-1}; Fig. 4c).

Despite the relatively high chl *a* levels at stn 103 (>2 mg m^{-3}), DOC was low in the UML ($\sim$55 µmol C l^{-1}). Chl *a* and DOC were homogeneously distributed within the UML as well as in most of the stations with low DOC and chl *a*. This station had a typical profile for the Bransfield Strait. The average DOC in the UML for this area

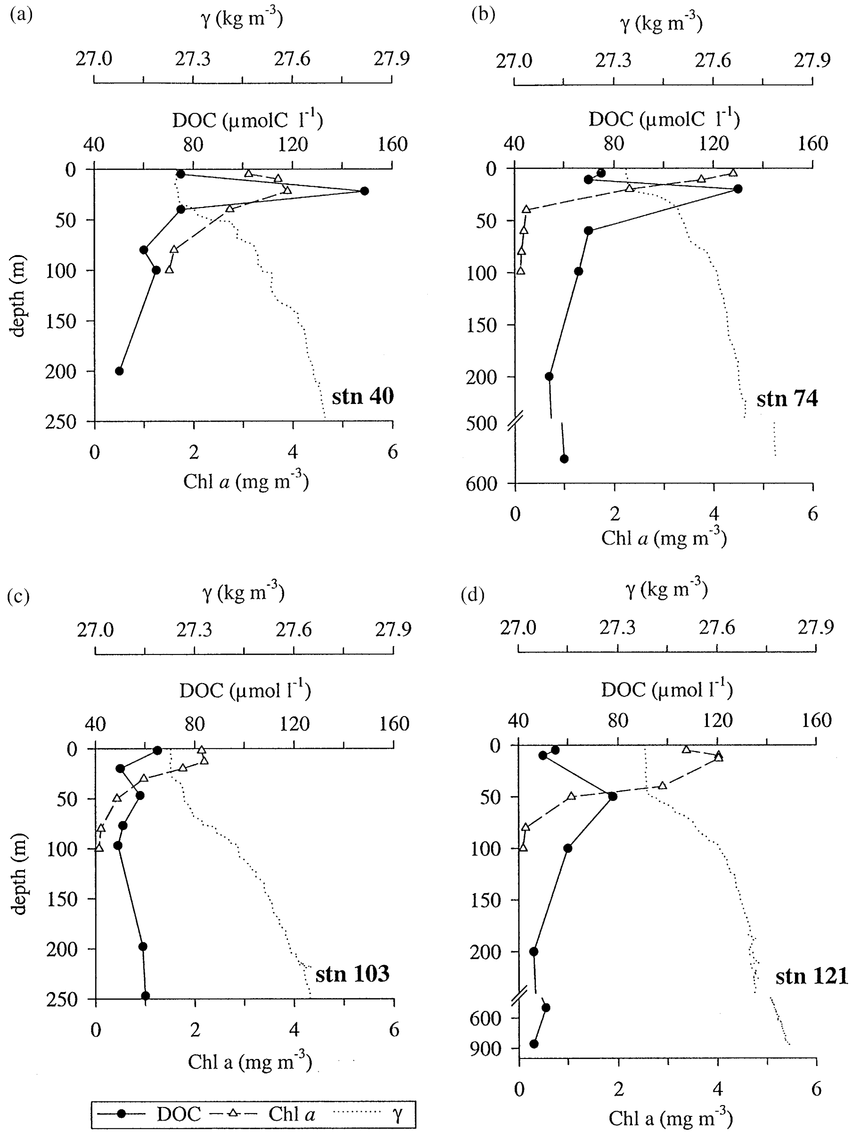

Fig. 3. DOC (μmol l^{-1}), sigma theta (γ; kg m^{-3}) and chl *a* (mg m^{-3}) vertical profiles at selected stations in the studied area: (a) stn 40, (b) stn 74, (c) stn 103 and (d) stn 121.

varied between 52 and 63 μmol C l^{-1} except in a few stations located near the islands (Fig. 4c). In contrast, most of the stations with high average values of DOC (for example: stns 40, 72, 121) showed no uniform profiles within the UML, which indicates net production processes being quicker than the time for homogenization.

Below the UML, DOC concentration decreases monotonically with depth, although several shelf and slope stations showed a slight increase of 5–10 μmol C l^{-1} in the bottom layer (stns: 39, 97, 99, 103 and 117). Several authors have obtained the same behavior for slope and abyssal stations (Williams et al., 1980; X. A. Álvarez-Salgado and

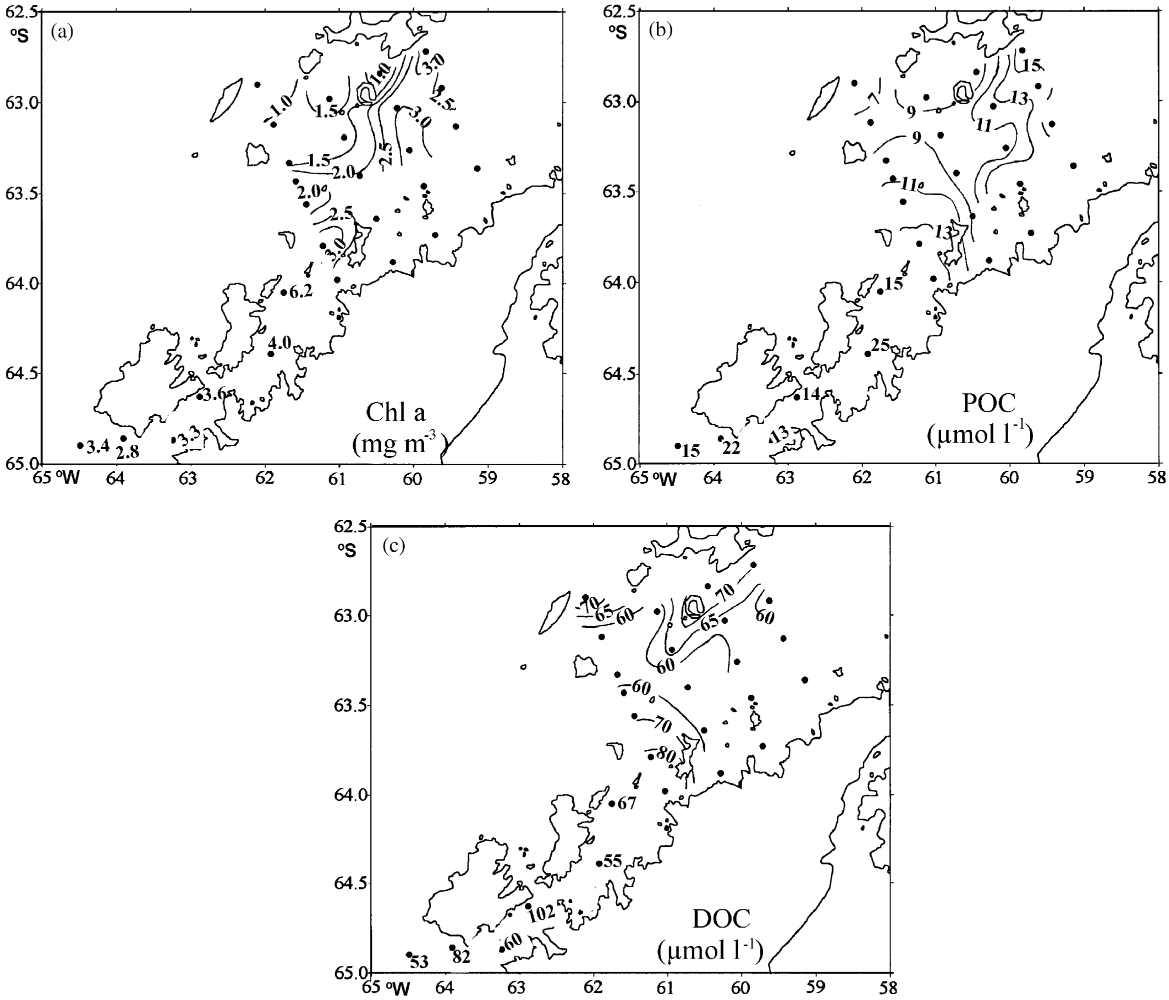

Fig. 4. Spatial distribution of depth integrated in the upper mixed layer (a) chlorophyll (mg m^{-3}), (b) POC (μmol l^{-1}) and (c) DOC (μmol l^{-1}).

A. E. J. M Miller, unpublished), which can be related to diffusion from the sediments of DOM younger than that in the overlying water (Bauer et al., 1995).

3.3. Organic matter below the upper mixed layer

A constant DOC concentration of 44 ± 4 μmol C l^{-1} ($n = 15$) was found below 400 m as a result of the homogeneous water mass there and the low bacterial activity at this depth range (Pedrós-Alió et al., 2002). This can be considered refractory DOC. It was similar to the DOC levels found by Kähler et al. (1997) in 6°W between 47° and 60°S, and by Carlson et al. (1998) in the Ross Sea. This concentration is intermediate between the low levels recorded in the deep Pacific Ocean (34–40 μmol C l^{-1}) and the higher levels measured in the deep Atlantic Ocean (~44–48 μmol C l^{-1}; Hansell and Carlson, 1998b). Our baseline DOC is very close to the values reported by these authors for the Southern Ocean (about 42 μmol C l^{-1}).

Following the distribution of silicate at the 200 m layer (Fig 2c), DOC concentrations were studied to check the influence of the different water masses. The values of DOC at this depth showed an average DOC concentration of 52 ± 7 μmol C l^{-1}, i.e. only 8 μmol C l^{-1} higher that the mean refractory DOC below 400 m. DOC values were not significantly different between CDW and BDW (t (df = 14) = 0.62, $p = 0.55$). The correlation coefficient between DOC and silicate was only $r^2 = 0.25$ ($p < 0.001$).

The fact that the DOC concentration at 200 m depth was mainly independent of water mass, indicates that the amount of DOC seems to be essentially refractory, although a minor fraction of semi-labile DOC (15% of total DOC) was also present at this depth.

3.4. *Organic matter in the upper mixed layer: the DOC excess*

The distributions of average chl *a* and POC (Fig. 4a and b) in the UML were quite similar. Maximum values were located in the Gerlache Strait (4–6 mg chl $a\,m^{-3}$ and 22–25 μmol C l^{-1}), and at several stations in the Bransfield Strait: at the Bransfield Front (>3.0 mg chl $a\,m^{-3}$, >12 μmol C l^{-1}) and at stratified stations (119 and 140 : 3 mg chl $a\,m^{-3}$, 16 μmol C l^{-1}). Minimum values corresponded to stations located north of the Bransfield Front (1.5 mg chl $a\,m^{-3}$, <9 μmol C l^{-1}). Although not all POC and chl *a* maxima coincided, the direct correlation (Model II; Sockal and Rolhf, 1995) between these variables for all samples (in the UML) of the study area was:

$$POC(\pm 3.9) = 2.5(\pm 0.3) + 4.3(\pm 0.3)\text{chl}\,a, \qquad (1)$$

$r^2 = 0.75$, $n = 50$, $p < 0.001$.

The high correlation between POC and chl *a* (Eq. (1)) allows us to estimate the percentage of authotrophs by multiplying the slope of the regression by the average chl *a* and dividing by the average POC. Authotrophs represent ~80% of POC in the UML. The slope of Eq. (1), 4.3 mol C g chl a^{-1} (51.6 g C g chl a^{-1}), was similar to the ratio used in the RACER program and is considered typical for Antarctic phytoplankton (Mitchell and Holm-Hansen, 1991). The range of POC/chl *a* ratios found in this layer (32–192 g C g chl a^{-1}) was within the values reported for Antarctic waters (between 11 and 416 g C g chl a^{-1}) by Palmisano et al. (1985) and El-Sayed and Taguchi (1981).

POC and PON were obviously coupled in the whole water column, and the direct correlation (Model II) was very high ($r^2 = 0.95$; $p < 0.001$). If we consider the UML, the direct correlation (Model II) between POC and PON for the study area was:

$$POC(\pm 0.6) = 0.35(\pm 0.17) + 5.1(\pm 0.1)PON, \qquad (2)$$

$r^2 = 0.97$, $n = 54$, $p < 0.001$.

The slope of Eq. (2) is lower than the Redfield ratio and similar to that found in Antarctic waters (Copin-Montégut and Copin-Montégut, 1983; Pérez et al., 1994). This low C/N ratio suggests that the environmental conditions were favorable for phytoplankton growth, as bacterial biomass (low C/N ratios) made a little fraction of particulate organic matter (Pedrós-Alió et al., 2002). The direct C/N ratio of POM was 5.3 ± 0.5 within the UML. These low POC/chl *a* and POC/PON ratios are typical of autotrophic systems (Holm-Hansen et al., 1989; Nelson et al., 1989).

The horizontal distribution of average DOC in the UML (Fig. 4c) showed maximum values in the Gerlache Strait (82 and 102 μmol C l^{-1}) and in the Gerlache–Bransfield confluence (86 and 99 μmol C l^{-1}), coinciding with relatively high chl *a* maximum values (>3 mg m^{-3}). Minimum values of average DOC were measured within the Bransfield Strait, especially at stations far from the island shelf (52–63 μmol C l^{-1}). The direct relation (Model II) between DOC and POC or chl *a* was only significant ($r^2 = 0.25$) in the Gerlache Strait and Gerlache–Bransfield confluence. In these two areas a higher correlation was found between total organic carbon (TOC = DOC + POC) and POC ($r^2 = 0.45$).

An excess of DOC was observed in surface waters as compared to bottom waters (background DOC: 44 ± 4 μmol C l^{-1}). The great variability of the average DOC in the UML leads to a large range of excess DOC (8–58 μmol C l^{-1}), with a mean value of $+22 \pm 13$ μmol C l^{-1} (average integrated DOC excess in the UML: 6.7 ± 7.0 g C m^{-2})

Table 1
Average and standard deviation of the depth-integrated excess DOC (DOCex = DOC_{UML}–44; mol C l^{-1}), POC (μmol C l^{-1}) and excessDOC/(excessDOC + POC) ratio in the UML; DOC production from phytoplankton (DOCpr; mg C m^{-3} h^{-1}) and percentage of extracellular release (PER) at 5 m (taken from Morán and Estrada, 2002) for the three areas considered: Gerlache Strait (Gerlache S.); Gerlache–Bransfield confluence (Gerl.–Bransf. conf.) and Bransfield Strait (Bransfield S.)[a]

Region	DOCex (μmol C l^{-1})	POC (μmol C l^{-1})	DOCex/ (DOCex + POC)	DOCpr (mg C m^{-3} h^{-1})	Per (%)
Gerlache S.	27 ± 18	17.8 ± 4.7	0.55 ± 0.16	2.33	13
Gerl.–Bransf. conf.	36 ± 13	17.4 ± 5.0	0.64 ± 0.11	0.85	17
Bransfield S.	17 ± 6	11.9 ± 4.1	0.57 ± 0.10	1.33	26

[a] *Note*: The stations sampled for DOC within the three regions were: Gerlache Strait: 34, 37, 39, 40, 43, Gerlache–Bransfield confluence: 47, 72, 74, Bransfield Strait: 52, 76, 79, 81, 94, 97, 99, 101, 103, 115, 117, 119, 121, 123, 138, 140, 142, 144.

for the whole study area. So, 15–57% of the observed DOC in this layer was semi-labile and labile DOC. The average excess DOC for the three contrasting region, Gerlache Strait, Gerlache–Bransfield confluence, and Bransfield Strait, varied between 17 and 36 μmol C l^{-1} (6 and 10 gC m^{-2}; Table 1).

The great variability of the excess DOC is larger than recently found in other systems, e.g. the Mediterranean Sea (0–40 μmol C l^{-1}; Copin-Montégut and Avril, 1993) or the Pacific Ocean (20–40 μmol C l^{-1}; Peltzer and Hayward, 1996; Hansell and Waterhouse, 1997), and similar to that found in coastal upwelling areas as the NW Iberian coast (10–60 μmol C l^{-1}; Doval et al., 1997) or the Arabian Sea (20–60 μmol C l^{-1}; Hansell and Peltzer, 1998). We can group the DOC data in two different areas: (A) Gerlache and Gerlache–Bransfield confluence (8 stations): relative high DOC concentrations; and (B) Bransfield Strait (18 stations): low DOC concentrations. The behavior of DOC was different in the recent study of Kähler et al. (1997) using the same HTCO method in the eastern Weddell Sea. He did not find any variability of surface DOC concentration because DOC was not dependent on biological activity. The range of DOC in the Bransfield Strait was similar to that found by Carlson et al. (1998) in the Ross Sea, where the low but labile surface DOC seems quickly recycled by bacterioplankton.

The average POC in the UML was 13.6 ± 5.1 μmol C l^{-1}. Therefore, the average excess DOC/(excessDOC + POC) was 0.59; i.e. 59% of the 'potentially' degradable organic matter is in the dissolved form and 41% as suspended particles (Table 1). The average percentage was close to 40–50% reported for the NW Iberian upwelling system (Doval et al., 1997), and far from an oligotrophic system as the Mediterranean Sea (89% after seasonal accumulation; Copin-Montégut and Avril, 1993).

3.5. *Origin and fate of the DOC excess*

The main sources of the excess DOC in the study area could be: extracellular release by phytoplankton, sloppy-feeding by zooplankton, and dissolution of fecal pellets, egestion by microzooplankton and cell lysis from viral infection (Carlson and Ducklow, 1995).

Melting ice did not seem to affect the DOC levels in the study area. Although stns 94 and 115 at the Bransfield Strait and stns 34 and 43 at the Gerlache Strait showed lower salinity values (< 33.8), they did not show high DOC levels, in contrast with the results found by Kähler et al. (1997) in other areas of the Southern Ocean.

In agreement with studies made during the RACER program, phytoplankton seems to be the dominant microplankton community during this cruise (Varela et al., 2002). Integrated zooplankton biomass between the surface and 200 m ranged from 0.19 to 0.99 g C m^{-2}. Although there is no direct correlation between the integrated zooplankton biomass and integrated DOC in the UML in the study area, maximum integrated zooplankton biomass were located in the Gerlache Strait, coinciding with maximum values of DOC (Cabal et al., 2002). Bacterial biomass was low compared to phytoplankton biomass (<25%; Pedrós-Alió et al., 2002) probably due to the low temperature and virus lysis (Pedrós-Alió et al., 2002).

Average DOC production from phytoplankton at 5 m was between 0.4 and 4.1 mg $\mathrm{C\,m^{-3}\,h^{-1}}$ for the whole study area (Morán and Estrada, 2002). The average values for the three selected regions (assuming they are similar throughout the UML) were: Gerlache Strait (2.33 mg $\mathrm{C\,m^{-3}\,h^{-1}}$), Gerlache–Bransfield confluence (0.85 mg $\mathrm{C\,m^{-3}\,h^{-1}}$), and Bransfield Strait (1.33 mg $\mathrm{C\,m^{-3}\,h^{-1}}$). The average excess DOC could be produced from phytoplankton in about 6, 21 and 6 days, respectively, if the losses were negligible. The estimated average geostrophic velocity in the Bransfield Current was 0.085 $\mathrm{m\,s^{-1}}$ during this cruise (Gomis et al., 2002), i.e. a flushing time of $\sim$15 days within the sampling area. If the UML is maintained during the flushing time, the excess DOC of most of the stations sampled (regions A and C, 89% of the total stations) could be produced by phytoplankton. The higher DOC found at Gerlache Strait and Gerlache–Bransfield confluence seems to be the result of a rapid biological production. A slow production but large flushing time favored DOC accumulation in the oceanic oligotrophic gyres (Copin-Montégut and Avril, 1993). The considerable time necessary to produce DOC within the Gerlache–Bransfield confluence from phytoplankton (21 days) suggests that the advection from Gerlache is quite important.

Low bacterial biomass contributed to the observed DOC accumulation in the UML. This accumulated DOC can be coagulate and aggregate to POC, as suggested by Karl et al. (1991a), or can be exported horizontally and/or vertically. Turbulent diffusion is the major mechanism for the downward transport of DOC from surface to deep waters, although stratification maintains the UML. The eddy diffusion flux of DOC from the UML to the waters below 400 m depth can be roughly estimated from $F = -K_Z\Delta\mathrm{DOC}/\Delta Z$ (Copin-Montégut and Avril, 1993). K_Z is the turbulent diffusion coefficient, which can be calculated by the equation $K_Z = \varepsilon N^{-2}R/(1-R)$. The dissipation rate ($\varepsilon$) and the Richardson number (R) have been set to constant values of $10^{-8}\,\mathrm{m^2\,s^{-3}}$ and 0.2, respectively, for the open ocean (Copin-Montégut and Avril, 1993). Consequently, K_Z mainly depends on the square of the Brunt–Väisälä freqquency, $N^2 = (g/\rho)(\mathrm{d}\rho/\mathrm{d}Z)$. Values of K_Z ranged from 5.5 to 19.7 $\mathrm{m^2\,d^{-1}}$. $\Delta\mathrm{DOC}/\Delta Z$ was simply calculated as $-(\mathrm{DOC_{UML}} - \mathrm{DOC_{UML-400}})/[(400 - Z_{\mathrm{UML}})/2 - (Z_{\mathrm{UML}}/2)]$ and varied from 0 to 11.8 mg $\mathrm{C\,m^{-4}}$. Finally, the resulting eddy diffusion fluxes ranged from 0 to 155 mg $\mathrm{C\,m^{-2}\,d^{-1}}$ (average: 30.3 mg $\mathrm{C\,m^{-2}\,d^{-1}}$). These numbers are extremely low when compared with the average excess DOC observed in the UML (6.7 g $\mathrm{C\,m^{-2}}$), confirming that stability, although small, keeps the DOC within the UML, indicating that turbulent diffusion is not an important route to inject semi-labile DOC in subsurface waters. Therefore, horizontal export seems to be the main fate of the excess DOC in the study area.

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References

Aristegui, J., Montero, M.F., 1995. Plankton community respiration in Bransfield Strait (Antarctic Ocean) during austral spring. Journal of Plankton Research 17, 1647–1659.

Aristegui, J., Montero, M.F., Ballesteros, S., Basterretxea, G., van lenning, K., 1996. Planktonic primary production and microbial respiration measured by 14C assimilation and dissolved oxygen changes in coastal waters of the Antarctic peninsula during austral summer: implications for carbon flux studies. Marine Ecology Progress Series 132, 191–201.

Bauer, J.E., Reimers, C.E., Druffel, E.R.M., Williams, P.M., 1995. Isotopic constraints on carbon exchange between deep ocean sediments and seawater. Nature 373, 686–689.

Cabal, J.A., Alvarez-Marqués, F., Acuña, J.L., Quevedo, M., Gonzalez-Quirós, R., Huskin, I., Fernández, D., Rodríguez del Valle, C., Anadón, R., 2002. Mesozooplankton distribution and grazing during the productive season in the Northwest Antarctic Peninsula (FRUELA cruises). Deep-Sea Research II 49, 869–882.

Carlson, C.A., Ducklow, H.W., 1995. Dissolved organic carbon in the upper ocean of the Central Equatorial Pacific Ocean, 1992: daily and finescale vertical variations. Deep-Sea Research II 42, 639–656.

Carlson, C.A., Ducklow, H.W, Michaels, A.F., 1994. Annual flux of dissolved organic carbon. Nature 371, 405–408.

Carlson, C.A., Ducklow, H.W., Hansell, D.A., Smith, W.O., 1998. Differences in ecosystem dynamics between spring blooms in the Ross Sea polynya and the Sargasso Sea reflected by contrasts in dissolved and particulate organic carbon partitioning. Limnology and Oceanography 43, 375–386.

Castro, C.G., Ríos, A.F., Doval, M.D., Pérez, F.F., 2002. Nutrient utilization and chlorophyll distribution in the Atlantic sector of the Southern Ocean during Austral summer 1995–96. Deep-Sea Research II 49, 623–641.

Copin-Montégut, G., Avril, B., 1993. Vertical distribution and temporal variation of dissolved organic carbon in the North Western Mediterranean Sea. Deep-Sea Research I 40, 1963–1972.

Copin-Montégut, C., Copin-Montégut, G., 1983. Stoichiometry of carbon, nitrogen, and phosphorus in marine particulate matter. Deep-Sea Research I 30, 31–46.

Dafner, E.V., 1992. Dissolved organic carbon in waters of the polar frontal zone of the Atlantic Antarctic in the spring–summer season of 1988–1989. Marine Chemistry 37, 275–283.

Dafner, E.V., Selin, P.Y., 1995. Organic matter in waters of the SW Atlantic sector of the southern ocean. Geo Journal 35 (1), 71–77.

Dawson, R., Schramm, W., Bölter, M., 1985. Factors influencing the production, decomposition and distribution of organic and inorganic matter in Admiralty Bay, King George Island. In: Siegfried, W.R., Condy, P.R., Laws, R.M. (Eds.), Antarctic nutrient cycles and food webs. Springer, Berlin, pp. 109–114.

Doval, M.D., Hansell, D.A., 2000. Organic Carbon and Apparent Oxygen Utilization in the Western South Pacific and The Central Indian Oceans. Marine Chemistry 68, 249–264.

Doval, M.D., Álvarez-Salgado, X.A., Pérez, F.F., 1997. Dissolved organic matter in a temperate embayment affected by coastal upwelling. Marine Ecology Progress Series 157, 21–37.

El-Sayed, S.Z., Taguchi, S., 1981. Primary production and standing crop of phytoplankton along the ice-edge in the Weddell Sea. Deep-Sea Research 28A, 1017–1032.

García, M.A., Castro, C.G., Ríos, A.F., Doval, M.D., Rosón, G., Gomis, D., López, O., 2002. Water masses and distribution of physico-chemical properties in the Western Bransfield Strait and Gerlache Strait during Austral summer 1995–96. Deep-Sea Research II 49, 585–602.

Gomis, D., García, M.A., López, O., Pascual, A., 2002. Quasi-geostrophic 3D circulation and mass transport in the western Bransfield Strait during Austral summer 1995/96. Deep-Sea Research II 49, 603–621.

Hansell, D.A., Carlson, C.A., 1998a. Net community production of dissolved organic carbon. Global Biogeochemical Cycles 12, 443–453.

Hansell, D.A., Carlson, C.A., 1998b. Deep ocean gradients in concentration of dissolved organic carbon. Nature 395, 263–266.

Hansell, D.A., Peltzer, E.T., 1998. Spatial and temporal variations of total organic carbon in the Arabia Sea. Deep-Sea Research II 45, 2171–2193.

Hansell, D.A., Waterhouse, T.Y., 1997. Control of the distributions of organic carbon and nitrogen in the Eastern Pacific Ocean. Deep-Sea Research I 44, 843–857.

Holm-Hansen, O., Mitchell, B.G., 1991. Spatial and temporal distribution of phytoplankton and primary production in the Western Bransfield Strait region. Deep-Sea Research II 38, 961–981.

Holm-Hansen, O., Mitchell, B.G., Hewes, C.D., Karl, D.M., 1989. Phytoplankton blooms in the vicinity of Palmer Station, Antarctica. Polar Biology 10, 49–57.

Huntley, M., Karl, D.M., Niller, P., Holm-Hansen, O., 1991. Research on Antarctic coastal ecosystem rates (RACER): an interdisciplinary field experiment. Deep-Sea Research II 38, 911–943.

Kähler, P., Björnsen, P.K., Lochte, K., Antia, A., 1997. Dissolved organic matter and its utilization by bacteria during spring in the Southern Ocean. Deep-Sea Research II 44, 341–353.

Karl, D.M., 1991. Racer: research on Antarctic coastal ecosystem rates. Preface. Deep-Sea Research II 38, v–vii.

Karl, D.M., Tilbrook, D.B., Tien, G., 1991a. Seasonal coupling of organic matter production and particle flux in the Western Bransfield Strait, Antarctica. Deep-Sea Research II 38, 1097–1127.

Karl, D.M., Holm-Hansen, O., Taylor, G.T., Tien, G., Bird, D.F., 1991b. Microbial biomass and productivity in the Western Bransfield Strait, Antarctica during the 1986–87 austral summer. Deep-Sea Research II 38, 1029–1057.

Karl, D.M., Christian, J.R., Dore, J.E., Letelier, R.M., 1996. Microbiological oceanography in the region west of the Antarctic Peninsula: microbial dynamics, nitrogen cycle and carbon flux. Foundations for Ecological Research West of the Antarctic Peninsula. Antarctic Research Series 70, 303–332.

Legendre, L., Fèvre, J.Le, 1995. Microbial food webs and the export of biogenic carbon in the oceans. Aquatic Microbial Ecology 9, 69–77.

Mitchell, B.G., Holm-Hansen, O., 1991. Observations and modelling of the Antarctic phytoplankton crop in relation to mixing depth. Deep-Sea Research II 38, 981–1009.

Morán, X.A.G., Estrada, M., 2002. Phytoplankton DOC and POC production in the Bransfield and Gerlache Straits as derived from kinetic experiments of ^{14}C incorporation. Deep-Sea Research II 49, 769–786.

Nelson, D.M., Smith, W.O., Muench, R.D., Gordon, L.I., Sullivan, C.W., Husby, D.M., 1989. Particulate matter and nutrient distribution in the ice-edge zone of the Weddell Sea: relationship to hydrography during later summer. Deep-Sea Research 36, 191–209.

Niiler, P.P., Amos, A., Hu, J.H., 1991. Water masses and 200 m relative geostrophic circulation in the Western Bransfield Strait region. Deep-Sea Research II 38, 943–961.

Palmisano, A.C., Soohoo, J.B., Sullivan, C.W., 1985. Photosynthesis–irradiance relationships in sea ice microalgae from McMurdo Sound, Antarctica. Journal of Phycology 21, 341–346.

Pedrós-Alió, C., Vaqué, D., Guixa-Boixereu, N., Gasol, J.M., 2002. Prokaryotic plankton biomass and heterotrophic production in western Antarctic waters, during the 1995. 96 Austral summer. Deep-Sea Research II 49, 805–825.

Peltzer, E.T., Hayward, N.A., 1996. Spatial and temporal variability of total organic carbon along 140°W in the equatorial Pacific Ocean in 1992. Deep-Sea Research II 43, 1155–1180.

Pérez, F.F., Figueiras, F.G., Ríos, A.F., 1994. Nutrient depletion and particulate matter near the ice-edge in the Weddell Sea. Marine Ecology Progress Series 112, 143–153.

Priddle, J., Hawes, I., Cellis-Evans, J., Smith, T.J., 1986. Antarctic aquatic ecosystems as habitants for phytoplankton. Biological Reviews 61, 199–238.

Sockal, R.R, Rolhf, F.J., 1995. Biometry. Freeman and Company (Eds.), New York, 887pp.

Skoog, A., Wedborg, M., 1994. Organic carbon and humic substances in the Weddell Sea. Reports on Polar Research 135, 168–169.

Thingstad, T.F., Hagström, A., Rassoulzadegan, F., 1997. Accumulation of degradable DOC in surface waters: is it caused by a malfunctioning microbial loop? Limnology Oceanography 42, 398–404.

Varela, M., Fernandez, E., Serret, P., 2002. Size-fractionated phytoplankton biomass and primary production in the Gerlache and south Bransfield Straits (Antarctic Peninsula) in Austral summer 1995–1996. Deep-Sea Research II 49, 749–768.

Wedborg, M., Hoppema, M., Skoog, A., 1998. On the relation between organic and inorganic carbon in the Weddell Sea. Journal of Marine Systems 17, 59–76.

Wiebinga, C.J., De Baar, H.J.W., 1998. Determination of the distribution of dissolved organic carbon in the Indian sector of the Southern Ocean. Marine Chemistry 60, 185–201.

Williams, P.M., Carlucci, A.F., Olson, R., 1980. A deep profile of some biologically important properties in the Central North Pacific gyre. Oceanologica Acta 3, 471–476.

Yentsch, C.S., Menzel, D.W., 1963. A method for the determination of phytoplankton chlorophyll and phaephytin by fluorescence. Deep-Sea Research 10, 221–231.