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Deep-Sea Research I

## Dissolved organic matter cycling in the confluence of the Atlantic and Indian oceans south of Africa



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#### ABSTRACT

The boundary between the Atlantic and Indian sectors of the Southern Ocean is a key spot of the thermohaline circulation, where the following water masses mix up: Indian Central water (ICW), South Atlantic Central Water (SACW), Antarctic Intermediate Water (AAIW), Circumpolar Deep Water (CDW), North Atlantic Deep Water (NADW), Weddell Sea Deep Water (WSDW) and Antarctic Winter Water (WW). An optimum multiparameter analysis based on the distributions of potential temperature, salinity, NO  $(=O_2+9.3 \times NO_3)$  and silicate during the GoodHope 2004 (GH04) cruise allowed us to (i) define the realms of these water masses; (ii) obtain the water mass proportion weighted-average (archetypal) apparent oxygen utilization (AOU) and dissolved organic carbon (DOC) concentrations of each water mass; and (iii) estimate the contribution of DOC to the oxygen demand of the study area. WW represented only 5.2% of the water volume sampled during GH04, followed by WSDW with 10.8%, NADW with 12.7%, SACW with 15.3%, AAIW with 23.1% and CDW with 32.8%. The distributions of DOC and AOU were mainly explained by the mixing of archetypal concentrations of these variables,  $75 \pm 5\%$  and  $65 \pm 3\%$  respectively, which retained the variability due to the basin-scale mineralization from the formation area to the barycentre of each water mass along the GH04 line. DOC accounted for 26 + 2% and  $12\pm5\%$  of the oxygen demand of the meso- and bathypelagic ocean, respectively. Conversely, local mineralization processes, retained by the residuals of the archetypal concentrations of DOC and AOU, did not contribute to improve significantly the mixing model of DOC.

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#### 1. Introduction

The meridional overturning circulation (MOC) plays a major role in the distribution of heat and dissolved substances throughout

the world ocean. It carries warm upper ocean waters to the northern North Atlantic, where it sinks and the resulting cold and salty North Atlantic Deep Water (NADW) moves southwards with the Deep Western Boundary Current (DWBC) (Wüst, 1935; Mémery et al., 2000; Bryden et al., 2005). South of the Falkland Islands, the DWBC intercepts the Antarctic Circumpolar Current (ACC), which acts as a conveyor of physical and chemical properties of the deep waters of the Atlantic, Indian and Pacific oceans (De Ruijter et al., 1999; Cunningham et al., 2003), providing a regulation mechanism of the Earth climate system (Rintoul, 1991, 2006; Swart et al., 2008). The ACC is also fed by the Weddell Sea Deep Water (WSDW) that forms in the Weddell Gvre and contributes to ventilate the abyssal world ocean (Orsi et al., 1999; Tomczak and Liefrink, 2005). The mixing of NADW and WSDW in the ACC produces the Circumpolar Deep Water (CDW) (Broecker et al., 1985; Poisson and Chen, 1987; Onken, 1995). Ventilation at intermediate depths of the southern hemisphere is mainly attributable to Antarctic Intermediate Water (AAIW), which forms north of the Subantarctic Front and East of the Drake Passage by ventilation of Sub-Antarctic Mode Water (Piola and Georgi, 1981; England et al., 1993; Sorensen et al., 2001). The poor knowledge about the circulation and biogeochemistry of the ACC

Abbreviations: AAIW, Antarctic Intermediate Water; AAIW<sub>3</sub>, Antarctic Intermediate Water of 3 °C: AAIW<sub>5</sub>. Antarctic Intermediate Water of 5 °C: AC. Agulhas Current; ACC, Antarctic Circumpolar Current; AOU, Apparent oxygen utilization; CDW, Circumpolar Deep Water; DOC, Dissolved Organic Carbon; DWBC, Deep Western Boundary Current; GH04, GoodHope hydrographic line 2004; ICW, Indian Central Water; ICW13, ICW of 13 °C; ICW165, ICW of 16.5 °C; LAT, Latitude; LON, Longitude; MOC, Meridional Overturning Circulation; NADW, North Atlantic Deep Water; NADW2, NADW of 2 °C; NADW4.6, NADW of 4.6 °C; NNLS, Non-Negative Least Squares method; NO,  $=O_2 + R_N \times NO_3$ ; NPF, North Polar Front; OMP, Optimum Multiparameter Analysis; PF, Polar Front; R<sub>C</sub>, moles of O<sub>2</sub> consumed per mole of carbon produced;  $R_N$ , moles of  $O_2$  consumed per mole of nitrate produced; SACCF, South Antarctic Circumpolar Front; SACW, South Atlantic Central Water; SACW12, South Atlantic Central Water of 12 °C; SACW18, South Atlantic Central Water of 18 °C; SAF, Subantarctic Front; SD, Standard Deviation; STF, Subtropical Front; WT, Water Type; VOL, Volume; WOCE, World Ocean Circulation Experiment; WSDW, Weddell Sea Deep Water; WW, Winter Water; Z, Depth

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south of Africa triggered the international research programme BONUS-GOODHOPE (http://www.univ-brest.fr/IUEM/BONUS-GOODHOPE), which is the umbrella of the research cruise where the field data here presented was collected.

Dissolved organic carbon (DOC), amounting to  $662 \pm 32$  Pg C, constitutes the major reservoir of organic matter in the world ocean, being mainly biologically refractory (Hansell et al., 2012). The highest DOC concentrations (about 70  $\mu$ mol C kg<sup>-1</sup>) are found in the surface layer of the tropical and subtropical ocean (40°N-40°S), where the enhanced stratification favours its slow accumulation. Surface DOC concentrations are lower at higher latitudes because of the increased mixing with the DOC-poor waters of the ocean interior (Hansell et al., 2009). The DOC produced in the illuminated surface layer is transported downwards into the deep sea, particularly at the intermediate and deep water formation sites (Doval and Hansell, 2000; Hansell et al., 2012). Then, microbial consumption of the biologically degradable fraction of DOC, amounting to  $20 \pm 4$  Pg C, occurs in parallel to its transport within the MOC, contributing to the increasing oxygen demand in the deep sea in chorus with the increasing age of the deep water masses (Jiao et al., 2010; Chen, 2011; Hansell et al., 2009, 2012).

This study is focused on the impact of water masses mixing and mineralization processes on the distribution of DOC in the under sampled sector of Southern Ocean separating the African and Antarctic continents. To achieve this goal, we have used the field data collected during the cruise GoodHope 2004 (GH04) and carried out an optimum multiparameter analysis (OMP) of the water masses that mix south of Africa. We defined water mass realms and obtained the corresponding water mass mixing weighted-average DOC values, which retain the variability of DOC from the formation area of each water mass to the GH04 line, and its residuals, which retain the variability of DOC within the GH04 line.

#### 2. Material and methods

#### 2.1. The cruise

The cruise GH04 was carried out onboard R/V Akademik Vavilov from Cape Town (South Africa; 33.93°S, 17.82°E) on the 8th of November 2004 to Ushuaia (Argentina; 54.48°S, 68.18°W) on the 9th of December 2004. The last hydrographic station was occupied on the 23rd of November at 55°S, 0°E (Fig. 1).

The transect consisted of 72 stations and, following Gladyshev et al. (2008), it crossed the following fronts (Fig. 1): Subtropical Front (STF), located between 40.07 and 40.37°S; Subantarctic Front (SAF), between 44.12 and 44.4°S; North Polar Front (NPF), between 49.02 and 49.41°S; Polar Front (PF), between 50.36° and 50.88°S; and South Antarctic Circumpolar Current Front (SACCF), between 52.75° and 53.45°S. The Antarctic Circumpolar Current (ACC) was the dominant flow south of the STF. North of the STF, the transect crossed the Agulhas Current (AC), which transports Indian Central Water (ICW) into the South Atlantic, and the South Atlantic Current (SAC), which transports South Atlantic Central Water (SACW) into the South Indian Ocean (see Fig. 1).

At each hydrographic station, a SBE 911 plus CTD probe attached to a SBE 32 rosette sampler of 24 Niskin bottles of 12 L was dipped to continuously record the profile of temperature and conductivity and to collect water samples for the calibration of the CTD probe and for the analysis of dissolved oxygen and nutrient salts (nitrite, nitrate, phosphate and silicate). Moreover, every three stations (white dots in Fig. 1), water samples were taken for the determination of full-depth dissolved organic carbon profiles.



**Fig. 1.** Map showing the GH04 cruise track. The following fronts were crossed: Subtropical Front (STF), Subantartic Front (SAF), Polar Front (PF) and South Antarctic Circumpolar Current Front (SACCF). Their positions were identified by Gladyshev et al. (2008). Relevant currents are also depicted: Agulhas, Benguela, South Atlantic, and Antarctic Circumpolar. The dots indicate the position of the 72 stations occupied during the cruise. White dots indicate the stations where samples for dissolved organic carbon analysis were collected.

#### 2.2. Analytical methods

Salinity (*S*) measurements for the calibration of the conductivity sensor of the CTD were performed according to the recommendations of the World Ocean Circulation Experiment (WOCE) procedures, using a total of 323 water samples. The final CTD uncertainties were 0.001 °C, 0.002 pss and < 1 dbar, for potential temperature ( $\Theta$ ), *S* and pressure, respectively.

Dissolved oxygen ( $O_2$ ) was measured with an accuracy of  $\pm 2 \,\mu$ mol kg<sup>-1</sup> by the Winkler method. The apparent oxygen utilization (AOU= $O_{2sat}-O_2$ ) was calculated using the algorithm proposed by Benson and Krause (UNESCO, 1986) for oxygen saturation ( $O_{2sat}$ ). Nutrients salts were determined on board by colorimetric methods on a segmented flow analyser "Bran-Luebbe" (Germany) following the procedures of Hansen and Koroleff (1999). The quality of the physical and chemical data obtained during GH04 (dissolved oxygen and inorganic nutrients) was assessed within the CARINA project and the concentration of nitrate was corrected using a factor of 1.02 (see the results for the cruise 90AV20041104 in Hoppema et al., 2009).

Samples for the analysis of dissolved organic carbon (DOC) were passed through pre-combusted (4 h, 450 °C) GF/F filters in an all-glass filtration system under positive pressure of high-purity N<sub>2</sub>. The filtrate was collected in pre-combusted (12 h, 450 °C) glass ampoules of 10 mL acidified with H<sub>3</sub>PO<sub>4</sub> at 25% to pH < 2. The ampoules were heat sealed and stored in dark at 4 °C until analyses in the base laboratory. DOC was determined with a Shimadzu TOC 5000 (Japan) analyser working under the principle of catalytic oxidation at high temperature (680 °C), to oxidize the organic carbon into CO<sub>2</sub>, and subsequent detection by non-dispersive

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