Particulate organic carbon export across the Antarctic Circumpolar Current at 10ºE: Differences north and south of the Antarctic Polar Front

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ABSTRACT

The vertical distribution of ^{234}Th was measured along the 10ºE meridian between 44ºS and 53ºS in the Antarctic Circumpolar Current (ACC) during the austral summer of 2012. The overarching goal of this work was to estimate particulate organic carbon (POC) export across three fronts: The Sub-Antarctic Front (SAF), the Antarctic Polar Front (APF) and the Southern Polar Front (SPF). Steady state export fluxes of ^{234}Th in the upper 100 m ranged from 1600 to 2600 dpm m^{-2} d^{-1}, decreasing with increasing latitude. Using large particle (>53 μm) C/^{234}Th ratios, the ^{234}Th-derived POC fluxes at 100 m ranged from 25 to 41 mmol C m^{-2} d^{-1}. Observed C/^{234}Th ratios decreased with increasing depth north of the APF, while south of the APF, ratios remained similar or even increased with depth. These changes in C/^{234}Th ratios are likely due to differences in the food web. Indeed, satellite images, together with macronutrients and dissolved iron concentrations suggest two different planktonic community structures north and south of the APF. Our results indicate that higher ratios of POC flux at 100 m to primary production occurred in nanophytoplankton dominated surface waters, where primary production rates were lower. Satellite images prior to the expedition suggest that the higher export efficiencies obtained in the northern half of the transect may be the result of the decoupling between production and export (Buesseler 1998). Transfer efficiencies to 400 m, i.e. the fraction of exported POC that reached 400 m, were found to be higher in the south of the APF, where diatoms were dominant and salps largely abundant. This suggests different remineralization pathways of sinking particles, influencing the transfer efficiency of exported POC to depth.

1. INTRODUCTION

The Southern Ocean (SO) is a key component of Earth's climate through its pivotal role in the regulation of atmospheric carbon dioxide (CO_2) and nutrient supply to other ocean basins (Gruber et al., 2009; Landschützer et al., 2015; Sarmiento et al., 2004; Takahashi et al., 2009). The SO consists of several hydrographic and biogeochemical regions delimited by zonal fronts, mostly characterized by strong horizontal temperature and salinity gradients (Orsi et al., 1995; Pollard et al., 2002b; Whitworth and Nowlin, 1987). The region between the southern limit of the Antarctic Polar Front (APF) and the southern boundary of the Antarctic Circumpolar Current (ACC) is characterized by upwelling of nutrient- and CO_2-rich deep waters (Hoppema et al., 2000; Nowlin and Klinck, 1986; Tomczak and Godfrey, 2001) and as a consequence, high macronutrients concentrations occur in the surface waters with persistent high concentrations of unused nitrate in a sufficiently lit and stratified euphotic zone.

Several *in situ* artificial iron fertilization experiments have shown that the low phytoplankton concentrations and productivity within the SO are due to iron limitation (Boyd et al., 2007; Coale et al., 2004; Smetacek et al., 2012). Changes in SO iron input and the resulting increase in particulate carbon export to greater depths (through the "biological pump") are hypothesized to be responsible for an approximately 30 ppm decrease in atmospheric CO_2 during glacial periods (Aumont and Bopp, 2006; Köhler et al., 2005). A better understanding of the relationship between primary productivity and the efficiency of the biological carbon pump is thus required in order to determine past and present climate change impacts on the SO carbon cycle and atmospheric CO_2. Previous studies have shown that export of organic matter to the deep ocean is not necessarily proportional to primary production rates (e.g., Buesseler, 1998), and discrepancies exist between models and *in situ* measurements (Arrigo et al., 1998; Gruber et al., 2009; Maiti et al., 2013). Sediment traps have shown regional variations among the various circumpolar zones and zonal sectors in particulate organic carbon (POC) export to the deep sea (see Boyd and Trull, 2007 and

73 references therein). However, scarce spatial coverage of sediment traps studies, and the possible
74 biases associated with traps (mainly due to hydrodynamics and solubilization; Buesseler et al.,
75 2007; Usbeck et al., 2003) warrant the use of other complementary approaches to quantify the
76 spatial and temporal variability of the biological pump in the SO.

77 A widely applied approach to estimate particle export is the use of the radionuclide pair
78 $^{234}Th/^{238}U$. Thorium-234 is a naturally occurring, short-lived radionuclide ($T_{1/2}$ = 24.1 days)
79 produced by the alpha decay of ^{238}U ($T_{1/2}$ = 4.5 x 10^9 years). Due to its high particle affinity,
80 thorium is rapidly adsorbed onto particle surfaces (Moore and Millward, 1988). In contrast
81 uranium is conservative in oxic systems (Chen et al., 1986). Thus, the deviation of $^{234}Th/^{238}U$ from
82 unity can be used as a proxy for particle dynamics (e.g., formation and export) in the ocean
83 surface. Further, the half-life of ^{234}Th is similar to the time scales of processes that determine
84 particle dynamics in the ocean (such as the development of phytoplankton blooms), allowing for
85 fine-scale observations of particle export and remineralization.

86 The fronts of the ACC have been found to coincide with boundaries between regions of similar
87 phytoplankton biomass (Sokolov and Rintoul, 2007). Moreover, phytoplankton composition and
88 distribution appear to be strongly linked to physical zonation within the SO (Laubscher et al.,
89 1993; Read et al., 2002). Sediment records also reflect such boundaries, with large opal
90 accumulation found south of the APF (Geibert et al., 2005; Tréguer and De La Rocha, 2013), as a
91 consequence of spatial segregation of phytoplankton communities due to difference temperature
92 and nutrient regimes (Falkowski et al., 1998). This in turn also affects zooplankton community
93 composition and distribution (Hunt and Hosie, 2005; Pakhomov and McQuaid, 1996; Pollard et
94 al., 2002a) and their grazing dynamics. Thus, physical controls on biogeochemical zonation are
95 expected to influence the pelagic community structure, which will affect the composition of the
96 sinking particles, and hence the downward flux of organic matter (Korb et al., 2012; Quéguiner,
97 2013)

In this study, we present new estimates of late summer POC export flux for the Atlantic sector of the SO, along the 10ºE meridian, across four different frontal zones: the Sub-Antarctic zone (SAZ), the Polar Frontal Zone (PFZ), the Antarctic Zone (AZ), and the Southern Zone (SZ). Our aim is to assess how the physical boundaries and zonal biology affect the magnitude and the efficiency of surface POC export and its transfer efficiency to depth. To do so, we analyzed water column distributions of ^{234}Th, combined with the measured ratio of POC/^{234}Th (hereafter C/^{234}Th) in order to obtain POC export fluxes and examine their variability as a function of physical oceanographic conditions, primary productivity and planktonic community stocks and composition.

2. MATERIALS AND METHODS

Samples were collected along a meridional transect at 10ºE, between 44ºS to 53ºS, from the 11th to the 22nd of January, 2012 (Figure 1) within the framework of the Eddy-Pump survey during the R/V *Polarstern* cruise ANT-XXVIII/3 (Wolf-Gladrow, 2013).

2.1 Th-234

Six stations (St. 57, 63, 69, 75, 81 and 84) were sampled for total ^{234}Th using a CTD-rosette equipped with 12 L Niskin bottles (Figure 1f; Table 1). Seawater samples (4 L each) were collected at 12 discrete depths in the upper 500 m of the water column, acidified to pH <2 with nitric acid and spiked with a known amount of ^{230}Th. Samples were processed using the MnO_2 co-precipitation technique (Benitez-Nelson et al., 2001) and counted on board using a gas flow proportional low-level background beta counter (counting statistics <3%) (RISØ, Denmark). Samples were recounted after 5-7 months to determine background activities.

Th-230 recoveries were measured with an adaptation of the method described in Pike et al. (2005), where the column purification step was removed. Briefly, the MnO_2 precipitate was dissolved in 10 ml of 8M HNO_3/10% H_2O_2 solution and a known amount of ^{229}Th was added as a second yield

122 tracer. Samples were sonicated for 30 min and allowed to stand covered for 6 h. Once the filter
123 was dissolved, the remaining solution was evaporated to dryness and reconstructed to 5% HNO_3
124 and 0.08% HF and then filtered using Acrodisc 0.2 µm HT Tuffryn membrane syringe filters
125 (Whatman). An aliquot was then taken from the filtered solution and diluted with 2.2% HNO_3
126 before measuring the $^{230}Th/^{229}Th$ using ICP-MS. Average recoveries of 95 ± 5% were obtained (n
127 = 68). ^{238}U activities (in units of dpm L^{-1}) were determined from salinity data using the
128 relationship from Owens et al. (2011) where ^{238}U (± 0.047) = (0.0786 ± 0.00446) x S – (0.315 ±
129 0.158). Calibration for the relative efficiency of the detectors was carried out using ^{238}U standards.
130 Replicate deep water samples (2500 m) were collected at selected stations to confirm the
131 calibration, with a resulting $^{234}Th/^{238}U$ activity ratio of 1.05 ± 0.09 (n = 7), consistent with that
132 expected for secular equilibrium. Uncertainties for the ^{234}Th activity were calculated by
133 propagating errors associated with counting, calibration, background corrections and ^{238}U
134 activities and were always <10%. The laboratories where samples were processed and analyzed
135 participated in the intercomparision of ^{234}Th measurements in both water and particulate samples,
136 as part of the GEOTRACES inter-calibration program (Maiti et al., 2012).

137 ***2.2 Particulate samples***

138 Samples for analysis of particulate matter composition and particle associated ^{234}Th were collected
139 at 100 and 300 or 400 m depth using *in situ* pumps (ISP; *Challenger Oceanic*) equipped with 142
140 mm diameter filter holders. Samples were taken at the same stations as seawater ^{234}Th profiles,
141 except those at 46ºS and 50ºS. Between 840 and 1500 L seawater was filtered through 53 µm
142 pore-size Nitex screens. The particulate material was rinsed from the screen using filtered
143 seawater, collected in an acid-cleaned plastic beaker and stirred to homogenize the sample. A
144 volumetric fraction of the rinse solution, representing ~30% of the total volume, was filtered onto
145 pre-combusted 25 mm quartz filters (QMA, Millipore) for ^{234}Th analysis. Another aliquot of a
146 similar volume was also filtered through a pre-combusted QMA filter for POC and particulate

147 organic nitrogen (PON) analyses (see section 2.5). Filters were dried overnight at 50ºC. ^{234}Th
148 particulate samples were counted at sea and recounted for background activities 5-7 months later,
149 as was done for the water samples, with associated uncertainties <10%.

150 ***2.3 Dissolved Fe***

151 Five stations (St. 60, 70, 76, 81 and 84) were sampled for dissolved iron profiles (DFe) using
152 metal-free GO-FLO bottles attached to a Kevlar line, at 5 to 7 discrete depths between 20 and 300
153 m. The GO-FLO bottles were transferred to a clean plastic "bubble" where the atmosphere was
154 kept clean by over pressurization with filtered air. DFe samples (~ 60 mL) were collected in 60
155 mL LDPE bottles directly from the GO-FLO bottles using pressurized nitrogen and inline 0.2 μm
156 pore size sterile capsules (Sartobran 300).

157 Seawater DFe concentrations were determined onboard according to the voltammetric method
158 which is based on the electroactivity of iron complexed to DHN (Laglera et al., 2013). Briefly,
159 immediately after filtration, samples were spiked with 12 μL HCl (30%; Merk, Trace Select) per
160 10 mL seawater for a pH of 2.0 (NBS scale) and 30 μM of DHN (2,3-dihydroxynaphthalene).
161 After allowing equilibration for 24 h at room temperature, samples were spiked with 500 μL of a
162 BrO_3^-/POPSO solution, and adjusted to pH ~8.7 with NH_4OH (15%, UltraTrace, Sigma).
163 Analytical sensitivity was determined for each sample using two standard additions of 0.3 nM
164 iron. The settings of the voltammetric analysis and other additional information can be found in
165 Laglera et al. (2013).

166 ***2.4 Nutrients and dissolved oxygen***

167 Macronutrients were analyzed colorimetrically on board using a Technicon TRAACS 800 auto-
168 analyzer (Seal Analytical), according to Grasshoff et al. (1983) (for nitrate), Murphy and Riley
169 (1962) (for phosphate) and Strickland and Parsons (1968) (for silicate). Details regarding the
170 complete procedure are given in Hoppe et al. (this issue).

Vertical profiles of dissolved oxygen through the entire water column (at about 20 discrete depths) were determined at all stations along the section. Oxygen concentrations were measured using a standard automated Winkler technique with photometric endpoint detection. The precision as determined by the mean difference of duplicates was 0.7 μmol/kg, or better than 0.3% coefficient of variation.

2.5 POC and PON

POC and PON concentrations in the upper water column were measured on 1 to 2 L seawater samples collected directly from the Niskin bottles attached to the CTD-rosette at 7-8 discrete depths (between 10 and 200 m depth). Samples were filtered onto pre-combusted 25 mm diameter GFF filters and stored in pre-combusted glass petri dishes. After filtration, filters were dried overnight at 50°C and stored at -20°C for further analysis on land. Before analysis, samples were thawed at room temperature and a few drops of 0.1 M HCl were added to the filters to dissolve the particulate inorganic carbon. Filters were then dried overnight at 50°C. POC and PON concentrations on the ^{234}Th filters were also analyzed after beta counting for comparison with filters from the ISP measured directly for POC and PON, thus comparing two aliquots of the >53 μm size fraction, in order to assess within station variability. All POC and PON measurements were measured with an EuroVector Elemental Analyzer (Euroanalysator EA). Samples were corrected for C and N blanks (1.37 ± 0.03 μmol C and 0.20 ± 0.02 μmol N, respectively), and averaged <10% of each signal. Measurement variability based on reference standard measurements was 3.6% (N) and 1.9% (C) for the upper water column samples.

2.6 Chlorophyll a

2.6.1 Satellite data

In order to capture regional synoptic variability in surface biological processes, merged chlorophyll-*a* (Chl-a) data (ESACCI-OC-L3S product, ~4 km, version 2.0,

195 htp://www.oceancolour.org from the daily Ocean Colour Climate Change Initiative OC-CCI,
196 2015) was averaged over the time period of interest. The OC-CCI data product provides high
197 quality ocean color products combining the Medium Resolution Imaging Spectrometer (MERIS)
198 on Envisat, the Moderate resolution Imaging Spectrometer (MODIS) on the Aqua satellite and the
199 Sea-viewing Wide Field-of-view Sensor (SeaWiFS) on Orb-View-2 sensors. For the time frame of
200 this study only MERIS and MODIS data were available. Current data processing improves
201 limitations of ocean color remote sensing in polar regions due to low solar elevation and frequent
202 cloud cover. This is achieved by an improved atmospheric correction applied to MERIS data with
203 the Polymer algorithm (Steinmetz et al., 2011), and to MODIS data following the algorithm of
204 Gordon and Wang (1994) with several subsequent modifications and improvements according to
205 IOCCG (2010).

206 *2.6.2 In situ Chl-a*

207 Water samples for Chl-a determination by means of fluorometry (Chl-a_{FLUO}) were collected at 8
208 depths between 10 and 200 m. Samples were filtered onto 25 mm GFF filters and treated
209 following the method described in Hoppe et al. (this issue). Chl-a content was measured in a
210 Turner 10-AU fluorometer. Calibration of the fluorometer was carried out at the beginning and at
211 the end of the cruise, with results diverging by 2%. Chl-a content was calculated using the
212 equation given in Knap et al. (1996) using average parameter values from the two calibrations.

213 Chl-a concentrations were also determined by high performance liquid chromatography (HPLC;
214 Chl-a_{HPLC}). Water samples were filtered and shock-frozen in liquid nitrogen and stored at -80°C
215 until analysis in the home laboratory following the method of Barlow et al. (1997), as described in
216 detail in Cheah et al. (this issue). Chl-a_{HPLC} was calculated as the sum of concentrations of
217 monovinyl *a* and chlorophyllide *a* (divinyl chlorophyll *a* was below detection in all samples). Chl-
218 a inventories were determined to a depth of 100 m according to the method described by Morel
219 and Maritorena (2001).

As shown by Hoppe et al. (this issue), both Chl-a data sets (Chl-a_{HPLC} and Chl-a_{FLUO}) were very similar ($r^2 = 0.97$, $p < 0.001$, n = 104, Chl-a_{FLUO} = 0.990 * Chl-a_{HPLC} + 0.0837). Chl-a_{HPLC} data was used to derive primary production rates (see section 3.6).

2.7 Phytoplankton size class analyses

Three pigment-based phytoplankton size classes (micro-, nano-, and picophytoplankton) were estimated following the procedure as in Uitz et al. (2009), using defined marker pigment concentrations in relation to Chl-a_{HPLC}, which has been tested for the SO waters (e.g., Uitz et al., 2009). Microphytoplankton corresponds to phytoplankton with size >20 μm, nanophytoplankton between 2-20 μm, and picophytoplankton between 0.2-2 μm. Detailed description of the calculation is presented in Cheah et al. (this issue).

2.8 Zooplankton

Zooplankton samples were collected from the upper 250 m of the water column during double oblique tows using a Rectangular Midwater Trawl (RMT 1+8) equipped with 1 m^2 (0.33 mm mesh size) and 8 m^2 (4.5 mm mesh size) nets. RMT8 samples were representative of the macrozooplankton and RMT1 samples were representative of the mesozooplankton (Atkinson and Peck, 1990; Ward, 1989). A flowmeter (Hydro Bios, Kiel) was mounted in the mouth of the RMT8 to measure the water volume filtered. Net tows were conducted at a speed of 2 to 2.5 kn. RMT8 samples were preserved in a 4% formaldehyde and seawater solution. Specimens were identified to the species level, counted and measured. Dry weight biomass was calculated using known length-weight relationships (Mizdalski, 1988; E. Pakhomov, *unpublished data*). RMT1 samples were split and one half preserved in a 4% formaldehyde and seawater solution formalin, and the other half sieved, dried at 50^{o}C for 48 hours, and weighed for sample dry weight.

3. RESULTS

3.1 Hydrography: Fronts and water masses

Vertical meridional potential temperature (θ), salinity, potential density, oxygen, DFe and Chl-a_{FLUO} over the upper 500 m are shown in Figure 1. A detailed description of the hydrographic characteristics encountered along the 10°E transect is given in Strass et al. (this issue). The Sub-Antarctic Front (SAF), located at 46.5ºS, was identified by an abrupt southward decrease in surface temperature and salinity. The Antarctic Polar Front (APF), apparent at 49.3ºS based on density profiles, was also associated with the northernmost extent of the temperature minimum layer. Finally, at 52.5ºS, the Southern Polar Front (SPF) was defined by a strong increase in salinity and steep decrease in surface temperatures.

Also indicated in Figure 1 are the water masses sampled along the 10ºE transect (Strass et al., this issue). Antarctic Surface Waters (AASW) and Sub-Antarctic Surface Waters (SASW) occupied the upper ~100 m south of the SAF. Below the pycnocline, Antarctic Intermediate Water (AAIW), with its salinity minimum of 34.2, extended northward of the SAF below depths of 300 to 400 m, whereas Upper Circumpolar Deep Water (UCDW) (salinity = 34.75 and θ = 2ºC) was only found south of the SPF. North of the SAF, a subsurface salinity maximum was evident between 100 and 300 m. This feature likely originated farther north where it was subsequently displaced southward as an anticyclonic eddy (Strass et al., this issue). Previous observations of such subsurface lobes of saltier water indicate that this is a common feature of the Subtropical Frontal Zone, located farther north of this transect (Heath, 1976; Smythe-Wright et al., 1998). Poleward compensation of Ekman convergence has been suggested as the origin of these features (Heath, 1976), which were occasionally found as far south as 50ºS (Deacon, 1945).

3.2 Dissolved iron

DFe concentrations were generally low along the meridional transect, ranging from 0.08 to 0.33 nM in the upper 100 m and varied the major gradients of other ancillary parameters (Figure 1e and Figure S1). Highest concentrations were measured in the upper 25 m of the SAZ (44ºS-46ºS) decreasing southwards, with almost full depletion at ~50ºS. This corresponds to the area where the

highest Chl-a_{FLUO} values were also found (Figure 1f). Indeed, Chl-a_{FLUO} and DFe concentrations were significantly inversely correlated (Spearman correlation coefficient, $\rho = -0.83$, $p < 0.0001$, n = 21).

A subsurface increase of DFe was observed at 40 m at the two southernmost stations (81 and 84) as well as a layer (60-80 m) of depleted DFe (0.07-0.13 nM), that matched a deep Chl-a_{FLUO} maximum (~0.6 mg m^{-3}) (Figure 1e and 1f). At these same stations below 100 m, higher concentrations of DFe occurred, which were positively correlated with salinity and negatively correlated with oxygen (Pearson correlation coefficient, $r = 0.82$ and $\rho = -0.85$, respectively, $p < 0.01$, n = 9). Furthermore, these high DFe concentrations were associated with the highest concentrations of nitrate and phosphate measured along this section (>35 μM for nitrate and >2.4 μM for phosphate; data not shown). A subsurface maximum of DFe (80-200 m) was also observed in the SAZ, coinciding with a subsurface salinity maximum (Figures 1b, 1e).

3.3 ^{234}Th deficits and fluxes

Significant deficits of ^{234}Th relative to ^{238}U (up to ~45%) were found in the upper 100-200 m of the water column at all the stations (Figure 2), with lowest deficiencies (~25%) observed at the two southernmost stations (52ºS and 53ºS). Deficits were consistent with the primary production zone (PPZ), here defined as the depth where fluorescence is reduced to 10% of its maximum value (Owens et al., 2014; Table 1). No significant ^{234}Th excess was observed. At 300-350 m, an additional small depletion of ^{234}Th was measured at the two southernmost stations. This depletion was not considered when estimating fluxes at depth due to poor vertical resolution below 200 m.

Steady state water column ^{234}Th fluxes, derived from the integrated ^{234}Th deficits with respect to ^{238}U activities, were determined at three depths at each station (Table 3; Figure 3): i) the equilibrium depth (Eq. depth; i.e., first depth where there is no significant difference between ^{238}U and ^{234}Th activities within error; Table 1); ii) 100 m, for better comparison with literature values

293 and to match the shallow ISP deployment depth, and iii) 400 m to match the deep ISP deployment
294 depth and to examine flux attenuation with depth. Fluxes were calculated using a 1-D steady state
295 model (Coale and Bruland, 1985) and neglecting advective and diffusive fluxes. An estimate of
296 the magnitude of these fluxes is provided further below (see section 4.1). The fluxes at 100 m
297 ranged from 1560 to 2610 dpm m^{-2} d^{-1} (average 2100 ± 400 dpm m^{-2} d^{-1}). The equilibrium depth
298 was generally found at 150-200 m (except at 52ºS and 53ºS). These deeper ^{234}Th deficits
299 represented a 20 - 40% increase in the ^{234}Th flux estimates, compared to those at 100 m. Thus,
300 ^{234}Th flux estimates at the equilibrium depth ranged from 1560 to 3570 dpm m^{-2} d^{-1}, with an
301 average flux of 2600 ± 800 dpm m^{-2} d^{-1}. Similar fluxes were also obtained at 400 m, ranging from
302 1320 to 3090 dpm m^{-2} d^{-1} (average 2300 ± 720 dpm m^{-2} d^{-1}) (Table 3). ^{234}Th fluxes estimated at the
303 three depth horizons decreased with latitude (r^2 = 0.92, p = 0.010; r^2 = 0.89, p = 0.015 and r^2 =
304 0.89, p = 0.017; for fluxes at 100 m, at equilibrium depth and at 400 m, respectively).

305 ***3.4 Particulate samples: ^{234}Th, POC and PON concentrations and ratios***

306 Particulate (>53 μm particle size) ^{234}Th activities were 1 - 17% of the total ^{234}Th measured at 100
307 m, and were between 3-13 times higher than those measured at 400 m (<1% of total ^{234}Th) (Table
308 2). POC and PON concentrations were measured in two different filter sets, one where particulate
309 ^{234}Th was also analyzed (C_{Th} and N_{Th}) and the other for POC and PON analyses only (C_{CN} and
310 N_{CN}), to check for heterogeneity in sampling. The POC and PON concentrations measured on both
311 filter sets were similar, validating our measurements on the ^{234}Th filters used to obtain the C/^{234}Th
312 (C_{Th}) and N/^{234}Th (N_{Th}) ratios (C_{Th} = 0.91 * C_{CN} + 0.24 and N_{Th} = 0.90 * N_{CN} + 0.01; r = 0.99, p
313 <0.001 and n = 14 for both data sets).

314 POC and PON concentrations (from particles >53 μm) decreased with depth at all the stations
315 (Table 2). C/N ratios remained nearly constant with depth at the two southernmost stations
316 (change <4%), while they varied by a factor of about 2 north of the APF (Table 2). C/^{234}Th ratios
317 at 100 m ranged from 11 to 20 μmol C dpm^{-1} and from 4.6 to 25 μmol C dpm^{-1} at 400 m. North of

318 the APF, the C/^{234}Th ratios at 100 m were higher than the ratios at 400 m. At the southernmost
319 station, at 53°S, the ratio was found to be similar at both depths, and increasing with depth at 52ºS
320 (Table 2). N/^{234}Th ratios ranged from 1.1 to 3.3 µmol N dpm^{-1} at 100 m and from 0.49 to 4.9 µmol
321 N dpm^{-1} at 400 m. Due to time constrains, ISP could not be deployed at all stations (Figure 1f).
322 Therefore, in order to calculate POC and PON export fluxes at 46ºS and 50ºS (see section 3.5) we
323 used C/^{234}Th and N/^{234}Th ratios measured at stations at 44ºS and 52ºS, which belonged to the
324 same biogeochemical provinces, respectively (44ºS and 46ºS: SAZ; 50ºS and 52ºS AZ; Figure 1).

325 ***3.5 POC and PON fluxes***

326 POC and PON export fluxes were obtained by multiplying the ^{234}Th fluxes by the C(N)/^{234}Th
327 ratios of the particles collected with the ISP (Table 3). These export estimates are therefore based
328 on the assumption that the C(N)/^{234}Th ratios of particles >53 µm are representative of sinking
329 matter. The rationale for using this conversion factor is that in the SO, large particles, such as
330 diatoms and fecal pellets, are considered to be main drivers of the particulate export flux (Cavan et
331 al., 2015; Honjo et al., 2008; Laurenceau-Cornec et al., 2015; Rutgers van der Loeff et al., 2002).
332 Thus, one would expect particles >53 µm to be representative of the sinking material, rather than
333 smaller particle sizes. POC fluxes at 100 m ranged from 25 to 41 mmol C m^{-2} d^{-1}, with no clear
334 latitudinal variation (Figure 3). However, POC export flux estimates at 400 m, indicated enhanced
335 export in the southern half of the transect, whereas at the two northernmost stations significant
336 attenuation of the flux with depth was observed (Table 3; Figure 3). PON fluxes at 100 and 400 m
337 ranged from 2.4 to 7 mmol N m^{-2} d^{-1} and 1.4 to 13 mmol N m^{-2} d^{-1}, respectively, showing similar
338 patterns to the POC fluxes (Table 3). From 44ºS to 48ºS, POC and PON fluxes at the equilibrium
339 depth tended to be higher than at 100 m, ranging from 34 to 50 mmol C m^{-2} d^{-1} and 3.5 to 9 mmol
340 N m^{-2} d^{-1}, respectively, whereas in the southern half of the transect no significant differences were
341 observed between both depth (Table 3).

342 ***3.6 Derived primary production***

343 Measurements of *in situ* daily primary production using ^{14}C uptake (PP; see Hoppe et al., this
344 issue, for details) coincided with ^{234}Th sampling at only two stations (81 and 84). Therefore, we
345 used estimated primary production rates (PPRes). PPRes were derived from the relationship
346 between Chl-a_{HPLC} standing stock measurements in the upper 100 m of the water column (Chl-
347 a_{HPLC}_100m) and PP at 100 m from the stations sampled at ~12ºW (from 29 Jan to 17 Feb 2012;
348 data from Hoppe et al., this issue) and at stations 81 and 84 (C.J.M Hoppe, *unpublished data*): PP
349 = 232 + 13 * Chl-a_{HPLC}_100m (with PP expressed in mg C m^{-2} d^{-1}; $r^2 = 0.82$, $p < 0.001$, n = 11).
350 Using this equation, PPRes estimated for all stations had a mean relative deviation of -3% and a
351 standard deviation of 20% when compared to directly measured PP (n = 11). The derived PPRes
352 ranged from 54 to 86 mmol C m^{-2} d^{-1} (Table 3). The stations north of the APF showed
353 significantly lower PPRes than in the southern half of the transect (56 ± 3 mmol C m^{-2} d^{-1} *vs* 78 ±
354 7 mmol C m^{-2} d^{-1}).

355 ***3.7 Phytoplankton and zooplankton distribution***

356 Along the transect, a clear shift in phytoplankton communities was observed north and south of
357 the APF (Figure 6a, see also Cheah et al., this issue). Nanophytoplankton dominated north of the
358 APF, with microphytoplankton abundances <40%. South of the APF the phytoplankton
359 community was dominated by microphytoplankton (>60%). Picophytoplankton represented <10%
360 along the entire transect.

361 Total mesozooplankton biomass was an average of 45% higher than macrozooplankton biomass
362 across the transect (Figure 6b). An exception was at 52ºS where the macrozooplankton biomass
363 was inflated by a large ctenophore catch. Mesozooplankton biomass was elevated in the vicinity of
364 the APF, but no clear difference was observed between the areas to the north and south of this
365 front. Macrozooplanton biomass tended to be higher south of the APF, but stations with
366 comparable biomass were recorded north of the APF. Overall, the macroplankton community
367 north of the APF was dominated (in order of numerical importance) by chaetognaths (54%), while

368 south of the APF salps accounted for up to 91% of the numerical abundance (Figure 6c). A
369 detailed description of the zooplankton composition is presented in Hunt and Pakhomov (this
370 issue).

371 **4. DISCUSSION**

372 The SO has been previously described as "one of the ocean's most efficient biological pumps"
373 (Buesseler et al., 2001), although it has recently been suggested that on a global scale, its carbon
374 export potential might be lower than previously thought (Maiti et al., 2013). High POC export
375 fluxes (>20 mmol C m^{-2} d^{-1}) occurring in late austral spring/summer following phytoplankton
376 blooms have been observed repeatedly (Buesseler et al., 2003; Friedrich and Rutgers van der
377 Loeff, 2002; Savoye et al., 2008). Our estimates of ^{234}Th fluxes at 100 m (1560 to 2610 dpm m^{-2} d^{-1}) are within the mid to upper range of previously reported estimates (from negligible to 3800 dpm m^{-2} d^{-1}; on average 1660 ± 920 dpm m^{-2} d^{-1}, n = 201; Figure 4). Our Th-derived POC fluxes estimated along the 10ºE transect (25 to 41 mmol C m^{-2} d^{-1}) are, however, among the highest fluxes reported to date within the SO (from negligible to 91 mmol C m^{-2} d^{-1}; on average 13 ± 13 mmol C m^{-2} d^{-1}; n = 273; Figure 4; also see compilations by Maiti et al., 2013 and Le Moigne et al., 2013), and close to values found in areas with natural and artificially high iron inputs (e.g., Morris et al., 2007; Smetacek et al., 2012). This is surprising given that our measurements were conducted in open ocean areas of the ACC. In the following sections, the effects of physical processes are investigated in order to validate the 1-D steady state approach applied (section 4.1). The distribution of DFe is discussed relative to previous studies and with ^{234}Th activity profiles. Biological uptake and possible inputs linked to water masses are also explored (section 4.2). Variability in export along the transect is also examined in light of planktonic community structure in order to provide insight into the main drivers of POC export fluxes throughout the region (section 4.3), and how differences in food webs may affect POC export and transfer efficiencies to depth (section 4.4). Finally, a comparison with previous studies is also presented to

393 highlight the large variability within the SO, mainly linked to the timing and magnitude of the
394 phytoplankton blooms (section 4.5).

395 ***4.1 Physical transport processes: effect on ^{234}Th export fluxes***

396 Steady-state conditions were assumed to calculate ^{234}Th export fluxes as none of the stations were
397 revisited during the expedition. Previous studies have shown export fluxes to be relatively
398 constant over time in the study area during the austral summer, with no significant differences
399 between results obtained when applying steady and non-steady state conditions (Rutgers van der
400 Loeff et al., 2011, 2002). In general, in the open ocean, diffusion and advection are considered to
401 be negligible compared to the vertical downward flux of ^{234}Th on sinking particles (see review by
402 Savoye et al., 2006) except in strong upwelling areas (Buesseler et al., 1998). However, the study
403 area is located in a dynamic region characterized by three fronts where advective and diffusive
404 processes could be significant (Strass et al., this issue). For instance, Strass et al. (2002b) reported
405 mesoscale frontal dynamics that influenced chlorophyll distribution patterns, which were highly
406 correlated with other biological parameters, such as primary production (Strass et al., 2002a) and
407 zooplankton abundances (Pollard et al., 2002a). Therefore, we assessed the assumption of
408 negligible physical processes on our ^{234}Th flux calculations (see details in the supplementary
409 information). Our estimates indicate that, overall, the combination of advective and diffusive
410 fluxes would represent 7 - 17% of the ^{234}Th export fluxes at 100 m, comparable to their associated
411 uncertainties (6 - 12%). Therefore, by taking into account physical transport mechanisms, the
412 uncertainty of ^{234}Th export fluxes would increase to 10-21%, in agreement with previous results
413 presented by Resplandy et al. (2012), where errors due to the dynamic transport of ^{234}Th related to
414 small-scale structures were found to be $< 20\%$.

415 ***4.2 Dissolved Fe distributions***

416 The distribution of Chl-a in the SO is mainly regulated by inputs of new iron to the system

(Sokolov and Rintoul, 2007). DFe concentrations in the Atlantic sector of the ACC progressively decrease eastwards as the ACC moves from the main iron source (the Antarctic Peninsula and South Georgia, de Jong et al., 2012). Despite the high spatial variability shown here, our DFe data are in excellent agreement with the few prior sampling efforts carried out in this sector of the SO (Figure S1) (Chever et al., 2010; Klunder et al., 2011) suggesting that major features in DFe distributions are persistent during the austral summer.

Satellite images show high Chl-a concentrations (up to 1.3 mg m^{-3}) north of the APF about a month prior to the cruise (Figure 5; Figure S2). However, DFe concentrations in that area were not as depleted as in the central region of the transect during the cruise (Figure 1e). The biological uptake of DFe north of the APF might have been limited by silicate availability since silicate concentrations were in the range of limiting concentratrions, namely $\leq$ 1 µM (Figure 7) (Le Moigne et al., 2013a, Cheah et al., this issue). Additionally, the high salinity intrusion at 100-300 m supports a lateral advection of DFe (Figures 1b and 1e). During the cruise, the highest Chl-a concentrations (up to 1.2 mg m^{-3}; Figure S1) were measured between 49ºS and 52ºS (Figure 5e), leading to strong depletion of DFe in the upper 100 m. The low DFe values were probably caused by recent biological uptake and the subsequent removal through sinking particles. Biological uptake of DFe would explain its inverse correlation with Chl-a_{FLUO} (ρ = -0.83, p <0.0001, n = 21). In general, DFe and $^{234}Th/^{238}U$ profiles followed a similar trend with depth, and are inverse to Chl-a_{FLUO} profiles, with DFe depletion matching the increase of ^{234}Th deficits (Figure S1). This suggests that the process causing the reduction of DFe concentrations also affected the ^{234}Th deficits at a similar depth range. However, it should be noted that the gradient in ^{234}Th deficits are steeper than gradients in DFe (between ~60 - 200 m), probably due to a more rapid turnover of Fe than that of ^{234}Th, a finding also reported by Klunder et al. (2011).

The highest DFe concentrations were found in the southern part of the transect (St. 81 and 84), below ~300 m associated with UCDW waters, where oxygen concentrations were (<200 µmol kg^{-}

[1]) (Figure 1d). Indeed, DFe concentrations below 100 m were strongly correlated with salinity and negatively correlated with oxygen at those two stations ($\rho = 0.88$ for salinity and $\rho = -0.85$ for oxygen, with $p < 0.01$ and n = 9 for both correlations). Higher DFe concentrations have been found previously in UCDW waters (Klunder et al., 2011) and are typical of reduced oxygen concentrations due to an increase of iron solubilization during POC remineralization and stabilization of highly soluble Fe(II) (Millero et al., 1987). Low Chl-a_{FLUO} values despite high concentrations of all major nutrients at the southern end of the transect (Figure 7) indicate, however, that little of the DFe in UCDW waters reaches the photic layer.

4.3 Differences in planktonic community N-S of the APF: Effects on POC export and attenuation

SO fronts are physical boundaries that delimit zones of distinct physical, chemical, and biological properties (e.g., Read et al., 2002; Strass et al., 2002b) that in turn could regulate the particle export flux. In this study we did not observe a clear zonation related to the fronts regarding ^{234}Th export fluxes, although enhanced export was measured in areas where, as indicated by satellite imagery (Figure 5, Figure S2), phytoplankton blooms occurred and peaked about a month prior to our sampling (north of the APF). Since the ^{234}Th method integrates over time scales of several weeks, we could expect a decoupling between ^{234}Th deficiencies in the upper water column as compared to the biological parameters measured during the cruise (e.g., Chl-a concentrations or primary production) (Buesseler, 1998).

The POC export fluxes at 100 m were in the higher end of the range of previous reported estimates, mainly driven by high C/^{234}Th ratios (Figure 4). Further, contrary to ^{234}Th fluxes, POC fluxes were not correlated with latitude ($r^2 = 0.27$; $p = 0.29$; similar for PON fluxes: $r^2 = 0.08$; $p = 0.59$) (Figure 3). Differences between stations north and south of the APF were found when comparing changes in POC export fluxes at 100 and 400 m. Due to changes in C/^{234}Th ratios with depth, POC fluxes between 100 and 400 m depth showed higher attenuation north of the APF than

467 southern stations, which showed little to no attenuation (Figure 3; Table 3). C content in particles
468 varies due to particle volume and composition, whereas ^{234}Th is quickly adsorbed onto the
469 particles' surface sites (Santschi et al., 2006). As a consequence, first order dynamics predicts an
470 increase in C/^{234}Th ratio in large particles due to high volume:surface area ratios (Buesseler et al.,
471 2006). However, additional aspects of the biological community (e.g., dominant phytoplankton
472 group, bacterial activity, grazing, nutrient limitation) may also affect C content and C/^{234}Th ratios
473 in particles and their variation with depth (Buesseler et al., 2006; Jacquet et al., 2011; Puigcorbé et
474 al., 2015), leading to the large variability in C/^{234}Th ratios in particles (Figure 4; Buesseler et al.,
475 2006). Below we discuss the differences encountered north and south of the APF and their impact
476 on the POC export flux and attenuation (Table 4 summarizes the comparison between stations
477 north and south of the APF).

478 *4.3.1 North of the APF: small phytoplankton and higher particle attenuation*

479 In accordance with nutrient distribution (low Si north of the APF and low nitrate and phosphate
480 north of the SAF; Figure 7) planktonic communities north of the APF were dominated by
481 nanophytoplankton (mainly haptophytes; Cheah et al., this issue and Figure 6a) and had higher
482 abundances of carnivorous zooplankton (Hunt et al., this issue and Figure 6c). In this half of the
483 transect, a bloom took place a month prior to the sampling period (Figure 5; Figure S2). The
484 higher POC:Chla ratios found north of the APF also reflect communities in a later stage of
485 development with a larger fraction of heterotrophs or detritus (Figure 6d). Since the ^{234}Th
486 approach integrates over a period of time of a few weeks, the important ^{234}Th deficits observed at
487 the northern stations were most probably a consequence of that bloom, which might have been
488 dominated by larger phytoplankton groups, such as diatoms. However, during the sampling time
489 (post-bloom conditions), the small size of the dominant phytoplankton group (<20 μm), combined
490 with the lack of dense frustules and skeletons associated with diatoms, probably led to the
491 formation of a sinking particulate pool also dominated by small and more slowly sinking particles.
492 Both processes would allow more remineralization, which might explain the larger attenuation of

493 POC and ^{234}Th fluxes and C/^{234}Th ratios with depth in the northern half of the transect. The
494 differences observed in C/N ratios with depth at both stations also suggest alteration of the particle
495 composition with depth (Table 2). Overall, POC flux attenuation was observed north of the APF,
496 with up to a 74% decrease in flux between equilibrium depth and 400 m, although it should be
497 noted that vertical resolution below 200 m was poor.

498 *4.3.2 South of the APF: large phytoplankton and low attenuation*

499 In the southern half of the transect, south of the APF, higher nitrate and silicate concentrations
500 (Figure 7) favored larger phytoplankton, in particular diatoms (Figure 6a; Cheah et al., this issue).
501 The higher POC standing stocks combined with lower POC/Chl-a ratios (Figure 6d) indicate that
502 communities south of the APF had a higher proportion of phytoplankton relative to that observed
503 towards the north, where the bloom had occurred a month prior to our expedition (Figure 5). The
504 southern region was also likely subject to more intense grazing pressure due to higher abundances
505 of herbivorous zooplankton, mostly salps (Figure 6c). Pigment analyses also suggest that grazing
506 took place at those latitudes (Cheah et al., this issue). The structure of the diatom dominated
507 planktonic community in this area (including thickly silicified species characteristic of iron
508 deficient open ocean areas of the Southern Ocean; Assmy et al., 2013) and abundance of salps,
509 might have led to both retention of POC at the surface (Assmy et al., 2013; Iversen et al., this
510 issue) as well as production of a sinking particle pool constituted by large fast sinking particles
511 that were rapidly able to reach 400 m and only be minimally affected by remineralization (Rutgers
512 van der Loeff et al., 2002). Salps were 2-3 orders of magnitude more abundant at the southern
513 stations compared to northern stations (B.P.V. Hunt, *pers. comm.*). These large grazers can
514 produce fast sinking fecal pellets (200-2700 m d^{-1}, Bruland and Silver, 1981; Iversen et al., this
515 issue; Madin, 1982; Phillips et al., 2009; Turner, 2002) and have rapid defecation rates (Madin,
516 1982), making them potentially important contributors to POC export (Ebersbach and Trull, 2008;
517 Perissinotto and Pakhomov, 1998; Phillips et al., 2009; Smith et al., 2013). The additional
518 ballasting due to the inclusion of thickly silicified diatoms, such as *Fragilariopsis kerguelensis*

519 which dominated assemblages at station 84 (53ºS; Klaas, *unpublished*), may also increase the
520 sinking velocities of fecal pellets and aggregates (Francois et al., 2002; Klaas and Archer, 2002),
521 reducing their residence time in the upper ocean. This could help explain the small variation of the
522 C/N ratios and low/negligible POC flux attenuation with depth at the southernmost stations (Table
523 2).

524 Additional information regarding POC export south of the APF is derived from surface tethered
525 sediment traps deployed at 53ºS, at 100 and 400 m (Iversen *et al., unpublished data*). Differences
526 between both techniques (from water column ^{234}Th deficits versus POC export measured directly
527 from the sediment traps) are typically found in the literature to be within a factor of 2 to 4, partly
528 due to their time scale of collection (several weeks *vs* ~24 h), as well as methodological issues
529 between techniques (Buesseler, 1991). As such, both methods can be used to complement one
530 another. The particulate C/^{234}Th ratios collected using sediment traps were about a factor of 3
531 lower than those collected using ISP, although similar to ISP, the ratio did not change with
532 increasing depth (6.5 ± 0.5 and 6.9 ± 0.6 μmol C dpm^{-1}, at 100 and 400 m, respectively).
533 Sediment trap particles also contained a large presence of fecal pellets (MH. Iversen, *pers.*
534 *comm.*). While the lack of a change in C/^{234}Th ratios confirms the results obtained for ISP particles
535 (>53μm), the differences in magnitude of the C/^{234}Th ratios suggest that the POC fluxes estimated
536 using ISP particles represent an upper limit, at least at 53ºS. POC fluxes measured by sediment
537 traps at 53ºS (MH. Iversen *pers. comm*.) also show small flux attenuation with depth (36% and
538 11%, for sediment traps and the ^{234}Th method, respectively), again confirming the results obtained
539 with the ^{234}Th approach.

540 ***4.4 Export and transfer efficiencies***

541 Numerous studies have reported significant carbon export from the upper water column in the SO
542 based on a variety of methodological approaches (e.g., oxygen or nutrient mass balance, short-
543 lived radionuclides, sediment traps) and across different frontal regions (Buesseler et al., 2001;

544 Cochran et al., 2000; Friedrich and Rutgers van der Loeff, 2002; Hoppema et al., 2002; Rutgers
545 van der Loeff et al., 1997; Savoye et al., 2008; Schlitzer, 2002; Usbeck et al., 2003) and
546 productivity systems (Cavan et al., 2015; Ebersbach et al., 2011; Manno et al., 2015; Rembauville
547 et al., 2015a, 2015b; Salter et al., 2012). The overall emerging picture from these studies suggest
548 that in areas with high productivity downward transport of organic carbon is mainly driven by
549 blooms of diatoms (leading to the export of 30-50% of SO net primary production) with
550 zooplankton fecal material as a major pathway for exporting carbon to the deep ocean after the
551 major sedimentation pulse (diatom dominated spring bloom) in areas with low productivity
552 (Cavan et al., 2015; Laurenceau-Cornec et al., 2015; Manno et al., 2015; Rembauville et al.,
553 2015a)

554 In this study, export efficiencies were calculated by dividing the Th-derived POC fluxes at 100 m
555 by the PPRes. Higher export efficiencies were coincident with lower PPRes, i.e., north of the APF
556 (Table 3), similar to the results previously reported by Lam and Bishop, (2007), Maiti et al. (2013)
557 and Laurenceau-Cornec et al. (2015). Using the equation of Maiti et al., (2013) to obtain the
558 export efficiencies based on the PP (Export efficiency = -0.3482 * log(PP) + 1.2239; Figure 3a in
559 Maiti et al., 2013) we found good agreement with our data at stations 44ºS and 46ºS (ratios
560 between measured and derived export efficiency of 1.1 and 1.0, respectively), whereas for the
561 other stations, lower export efficiencies than predicted by the model of Maiti et al. (2013) were
562 obtained (average ratio between both estimates 0.71 ± 0.07; n = 4). The decoupling between the
563 peak of the productive period (before the cruise) and the timing of export (declining of productive
564 period; during the cruise) could be responsible for the higher export efficiencies (average 60%,
565 range 46-69%) measured north of the APF. Rutgers van der Loeff et al. (1997) found similar
566 results during an austral spring bloom where there was also a delay between the increase in
567 phytoplankton standing stocks and ^{234}Th depletion, similar to Buesseler et al. (2003), who reported
568 a delay between onset of production and export of up to 1 month. Export efficiencies south of the

APF were lower (max. 44%). A relatively small export efficiency (27%) was also confirmed south of the APF using sediment trap results deployed at 53ºS (MH. Iversen, *pers. comm.*).

Stations south of the APF, however, had the highest transfer efficiencies (i.e., the percentage of POC flux at the equilibrium depth that reaches 400 m), ranging between 89% and 148% (Table 3). As discussed previously, these high transfer efficiencies can be explained by fast-sinking and weakly attenuated sinking material, combined with the effect of diel vertical migration of zooplankton (Cavan et al., 2015). Alternatively, these high transfer efficiency might be due to an overestimate of our C/^{234}Th ratios based on particles >53 μm (not necessarily sinking particles). Differences in attenuation are, however, primarily due to the fact that, in strong contrast to stations north of the APF, C/^{234}Th ratios south of the APF do not change with depth. C/^{234}Th ratios in sediment trap material (measured only at 53ºS), although lower than the ratios obtained from ISP, also present no decrease with depth. A comparison of C/^{234}Th ratios from several trap deployments south of the APF during the same cruise (Roca-Martí et al., this issue) did not show a systematic bias for C/^{234}Th ratios for ISP collected material compared to trap collected material. Further, no large differences were observed in C/^{234}Th ratios between 100 m and 300 m, similar to our results. In Roca-Martí et al. (this issue), Chl-a and fucoxanthin were found to be efficiently transferred between 100 and 300 m indicating that these pigments were exported to 300 m with little to no breakdown. Results from Cedhagen et al. (2014), obtained during the same expedition, also corroborate these findings as large concentrations of algal pigments were observed in the cytoplasm of foraminifera collected at depths >4000 m. Moreover, at station 81 (52ºS; ~3500 m depth), Ruff et al. (2014) observed a large number of diatom frustules and intact fecal pellets in the top layers of the sediments, even down to 5 cm depth. Combined these studies suggest rapid transport of material to sediments using a variety of pathways.

4.5 Comparison with previous studies

A global compilation of ^{234}Th-derived POC export estimates by Le Moigne et al. (2013), available

in http://doi.pangaea.de/10.1594/PANGAEA.809717, contains a number of studies located in the SO (iron fertilization experiments not included). Considering all these studies together with the results from our expedition presented here and in Roca-Martí et al. (this issue), as well as Planchon et al. (2015), Rosengard et al. (2015) and Savoye et al. (2008), we observed wide ranges in ^{234}Th export fluxes and C/^{234}Th ratios, with subsequent variability in the derived POC fluxes at 100 ± 10 m depth (Figure 4). This compilation, however, includes a variety of areas that are difficult to compare with our open ocean stations due to the large differences in phytoplankton assemblage and growth and biogeochemical aspects linked to their geographical location (e.g., ice coverage or Fe inputs from continental shelves). Therefore, here we only discuss our results together with studies conducted in the Atlantic sector of the open ACC (between 40ºS-60ºS and 15ºE-15ºW; see map inset in Figure 4) namely Planchon et al. (2013), Roca-Martí et al. (this issue), Rutgers van der Loeff et al. (2011, 2002, 1997) and Smetacek et al. (2012), outside the iron fertilization patch.

Except for the SO-JGOFS expedition (Rutgers van der Loeff et al., 1997), which was conducted during the austral spring (Oct-Nov 1992; 6ºE), all the studies discussed here were conducted during the austral summer (Dec-Jan) or late austral summer (Feb-Mar). During the austral spring, short but intense bloom events seem to contribute significantly to the annual C export. Data in Rutgers van der Loeff et al. (1997) supports this observation with a maximum ^{234}Th export flux of 3250 dpm m^{-2} d^{-1} at 100 m during a productive period of only 22 days and a POC flux at 100 m ranging from 19 to 38 mmol C m^{-2} d^{-1}, similar to the results observed during our study. Rutgers van der Loeff et al. (2002) reported constant export fluxes during a two week period of the austral summer three years later (1995/96). ^{234}Th and POC export fluxes at 100 m were 865 dpm m^{-2} d^{-1} and 8.8 mmol C m^{-2} d^{-1}, respectively. The magnitude of the fluxes presented by Rutgers van der Loeff et al. (2002) is similar to those reported by Planchon et al. (2013) during the Bonus GoodHope (BGH) expedition (Feb-Mar 2008), ranging from 870 to 1200 dpm m^{-2} d^{-1} and 2.3 to 5.1 mmol C m^{-2} d^{-1} for the section of their transect between 44ºS and 53ºS. This is almost 3 times

620 lower in ^{234}Th fluxes and about an order of magnitude smaller POC export fluxes than the
621 estimates calculated in our study. Rutgers van der Loeff et al. (2011) reported ^{234}Th fluxes along
622 the prime meridian (Feb 2008) that also decreased with increasing latitude, and were up to 1.6
623 times lower than the export fluxes from the current study at similar locations with respect to the
624 frontal systems. The maximum POC export fluxes estimated by Rutgers van der Loeff et al.
625 (2011) were 11 mmol C m^{-2} d^{-1} using the bulk of particles to obtain C/^{234}Th ratios, although this
626 value decreases by a factor of 2 when using >50 μm particles (5.4 mmol C m^{-2} d^{-1}). The
627 differences between both estimates highlight the importance that the particle composition has on
628 C/^{234}Th ratios and the necessity of properly sampling the particles that are contributing to the
629 export flux, which is still an open topic of discussion (Bishop et al., 2012; Durkin et al., 2015;
630 Puigcorbé et al., 2015). Smetacek et al. (2012) examined ^{234}Th and Th-derived POC fluxes outside
631 an iron fertilized patch (Feb-Mar 2004), with ~1600-2500 dpm m^{-2} d^{-1} and ~32-41 mmol C m^{-2} d^{-1},
632 close to the values reported here. Finally, Roca-Martí et al. (this issue) provide results from a
633 bloom at ~12ºW and ~51ºS during our expedition, where average ^{234}Th and Th-derived POC
634 export fluxes at 100 m were 2390 ± 340 dpm m^{-2} d^{-1} (n = 14) and 36 ± 15 mmol C m^{-2} d^{-1} (n = 9),
635 respectively.

636 The results from the 2012 Eddy-Pump survey presented here and in Roca-Martí et al. (this issue)
637 are comparable to the spring bloom export presented in Rutgers van der Loeff et al. (1997) and
638 also with the summer fluxes estimated by Smetacek et al. (2012) outside of the iron fertilized
639 patch. The main factor driving the differences between POC flux estimates are the C/^{234}Th ratios,
640 which were much lower during the 2008 expeditions (ranging from 1.7 to 4.8 μmol C dpm^{-1})
641 (Planchon et al., 2013 and Rutgers van der Loeff et al., 2011) than the ratios measured during this
642 study (16 ± 4 μmol C dpm^{-1}), in Roca-Martí et al. (this issue) (14 ± 3 μmol C dpm^{-1}) and in
643 Smetacek et al. (2012) (17 ± 3 μmol C dpm^{-1}).

644 As previously discussed, the planktonic community structure will affect the type and composition

645 of the particles generated in surface layers. Thus, the sampling time related to a bloom event (i.e.,
646 sampling prior, during or after a bloom) can lead to differences in the C/^{234}Th ratios measured.
647 High Chl-a concentrations (>1 mg m^{-3}) covering large areas can be observed from satellite images
648 during the sampling period of this expedition (Jan-Feb 2012; see also Figure 1 in Hoppe et al., this
649 issue) and in Smetacek et al. (2012), prior to iron fertilization. These features were minimal and
650 mainly located further west in Jan-Feb 2008 (see Figure 7 in Rutgers van der Loeff et al., 2011).
651 As suggested by Planchon et al. (2013) and Rutgers van der Loeff et al. (2011), the low fluxes
652 obtained during the 2008 expeditions were probably due to a post-bloom situation, where the
653 intensive export had already occurred and remineralization led to reduced POC export fluxes. Our
654 study was carried on earlier in the summer, probably during the late export phase where
655 remineralization is not able to compensate the ^{234}Th deficits created by the still present particle
656 export. Additionally, comparison between summers 2007/2008 and 2011/2012 using satellite
657 images (Figure S2) suggests that the higher export fluxes measured during 2012 were probably not
658 only a consequence of the sampling time but also due the larger magnitude of the bloom of that
659 year. Thus, not only the timing of sampling relative to the bloom, but also its magnitude, can
660 result in clearly different estimates of POC export fluxes, mainly due to the variability in the
661 C/^{234}Th ratios, even during the austral summer.

662 **5. CONCLUSIONS**

663 In this study, ^{234}Th was used as a tracer to estimate downward particle fluxes across the ACC in
664 order to examine the effect of hydrographic conditions, separated by fronts, on POC export, export
665 efficiencies and transfer efficiencies. ^{234}Th fluxes were higher in the northern part of the 10ºE
666 transect, due to a bloom that occurred about a month before our arrival, as revealed by satellite
667 images. POC fluxes at 100 m were relatively high (25 to 41 mmol C m^{-2} d^{-1}) and did not show
668 significant differences linked to the frontal zones. However, a major N-S shift in planktonic
669 community was reflected in the variation of the C/^{234}Th ratios with depth. Small phytoplankton

670 with low Chl-a concentrations dominated the transect north of the APF, whereas south of the APF
671 diatoms dominated the phytoplankton community, Chl-a was higher, and salps dominated the
672 macrozooplankton community. This probably resulted in sinking particle pools that differed in
673 their composition: aggregates of small particles in the north versus fast-sinking large particles in
674 the south. Export efficiencies were generally high (35 - 69%) partly due to a temporal decoupling
675 between production and export, with slightly higher values in the northern section, where derived
676 primary production rates were found to be lower and small phytoplankton dominant. On the other
677 hand, due to the absence of attenuation of the C/^{234}Th ratios with depth at the southern stations,
678 POC fluxes at 400 m were similar or even higher than at 100 m, which translates to high transfer
679 efficiencies in the region where diatoms and salps were more abundant.

680 Comparison with previous studies highlights the dynamic biological character of the study area,
681 with phytoplanktonic blooms of different magnitude that, together with the time elapsed between
682 the climax of the bloom and the sampling period, probably led to the differences observed
683 between studies, were large variability regarding C/^{234}Th ratios was observed. This supports the
684 use of combined techniques, such as sediment traps and the ^{234}Th-method, to estimate the
685 magnitude and composition of particle fluxes. Further efforts should be made in order to link the
686 planktonic community to variability of C/^{234}Th ratios, not just below the euphotic zone but also at
687 greater depths, in order to constrain the strength and efficiency of the biological pump in this
688 region.

689

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