1 **Particulate organic carbon export across the Antarctic Circumpolar Current at 10ºE:**

2 **Differences north and south of the Antarctic Polar Front**

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28   **ABSTRACT**

29   The vertical distribution of ^{234}Th was measured along the 10ºE meridian between 44ºS and 53ºS in

30   the Antarctic Circumpolar Current (ACC) during the austral summer of 2012. The overarching

31   goal of this work was to estimate particulate organic carbon (POC) export across three fronts: The

32   Sub-Antarctic Front (SAF), the Antarctic Polar Front (APF) and the Southern Polar Front (SPF).

33   Steady state export fluxes of ^{234}Th in the upper 100 m ranged from 1600 to 2600 dpm m^{-2} d^{-1},

34   decreasing with increasing latitude. Using large particle (>53 μm) C/^{234}Th ratios, the ^{234}Th-derived

35   POC fluxes at 100 m ranged from 25 to 41 mmol C m^{-2} d^{-1}. Observed C/^{234}Th ratios decreased

36   with increasing depth north of the APF, while south of the APF, ratios remained similar or even

37   increased with depth. These changes in C/^{234}Th ratios are likely due to differences in the food

38   web. Indeed, satellite images, together with macronutrients and dissolved iron concentrations

39   suggest two different planktonic community structures north and south of the APF. Our results

40   indicate that higher ratios of POC flux at 100 m to primary production occurred in

41   nanophytoplankton dominated surface waters, where primary production rates were lower.

42   Satellite images prior to the expedition suggest that the higher export efficiencies obtained in the

43   northern half of the transect may be the result of the decoupling between production and export

44   (Buesseler 1998). Transfer efficiencies to 400 m, i.e. the fraction of exported POC that reached

45   400 m, were found to be higher in the south of the APF, where diatoms were dominant and salps

46   largely abundant. This suggests different remineralization pathways of sinking particles,

47   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)

98 In this study, we present new estimates of late summer POC export flux for the Atlantic sector of

99 the SO, along the 10ºE meridian, across four different frontal zones: the Sub-Antarctic zone

100 (SAZ), the Polar Frontal Zone (PFZ), the Antarctic Zone (AZ), and the Southern Zone (SZ). Our

101 aim is to assess how the physical boundaries and zonal biology affect the magnitude and the

102 efficiency of surface POC export and its transfer efficiency to depth. To do so, we analyzed water

103 column distributions of ^{234}Th, combined with the measured ratio of POC/^{234}Th (hereafter C/^{234}Th)

104 in order to obtain POC export fluxes and examine their variability as a function of physical

105 oceanographic conditions, primary productivity and planktonic community stocks and

106 composition.

107 **2. MATERIALS AND METHODS**

108 Samples were collected along a meridional transect at 10ºE, between 44ºS to 53ºS, from the 11th to

109 the 22nd of January, 2012 (Figure 1) within the framework of the Eddy-Pump survey during the

110 R/V *Polarstern* cruise ANT-XXVIII/3 (Wolf-Gladrow, 2013).

111 *2.1 Th-234*

112 Six stations (St. 57, 63, 69, 75, 81 and 84) were sampled for total ^{234}Th using a CTD-rosette

113 equipped with 12 L Niskin bottles (Figure 1f; Table 1). Seawater samples (4 L each) were

114 collected at 12 discrete depths in the upper 500 m of the water column, acidified to pH <2 with

115 nitric acid and spiked with a known amount of ^{230}Th. Samples were processed using the MnO_2 co-

116 precipitation technique (Benitez-Nelson et al., 2001) and counted on board using a gas flow

117 proportional low-level background beta counter (counting statistics <3%) (RISØ, Denmark).

118 Samples were recounted after 5-7 months to determine background activities.

119 Th-230 recoveries were measured with an adaptation of the method described in Pike et al. (2005),

120 where the column purification step was removed. Briefly, the MnO_2 precipitate was dissolved in

121 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).

171   Vertical profiles of dissolved oxygen through the entire water column (at about 20 discrete depths)

172   were determined at all stations along the section. Oxygen concentrations were measured using a

173   standard automated Winkler technique with photometric endpoint detection. The precision as

174   determined by the mean difference of duplicates was 0.7 μmol/kg, or better than 0.3% coefficient

175   of variation.

176   ***2.5 POC and PON***

177   POC and PON concentrations in the upper water column were measured on 1 to 2 L seawater

178   samples collected directly from the Niskin bottles attached to the CTD-rosette at 7-8 discrete

179   depths (between 10 and 200 m depth). Samples were filtered onto pre-combusted 25 mm diameter

180   GFF filters and stored in pre-combusted glass petri dishes. After filtration, filters were dried

181   overnight at 50°C and stored at -20°C for further analysis on land. Before analysis, samples were

182   thawed at room temperature and a few drops of 0.1 M HCl were added to the filters to dissolve the

183   particulate inorganic carbon. Filters were then dried overnight at 50°C. POC and PON

184   concentrations on the ^{234}Th filters were also analyzed after beta counting for comparison with

185   filters from the ISP measured directly for POC and PON, thus comparing two aliquots of the >53

186   μm size fraction, in order to assess within station variability. All POC and PON measurements

187   were measured with an EuroVector Elemental Analyzer (Euroanalysator EA). Samples were

188   corrected for C and N blanks (1.37 ± 0.03 μmol C and 0.20 ± 0.02 μmol N, respectively), and

189   averaged <10% of each signal. Measurement variability based on reference standard

190   measurements was 3.6% (N) and 1.9% (C) for the upper water column samples.

191   ***2.6 Chlorophyll a***

192   *2.6.1 Satellite data*

193   In order to capture regional synoptic variability in surface biological processes, merged

194   chlorophyll-*a* (Chl-a) data (ESACCI-OC-L3S product, ~4 km, version 2.0,

195   http://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).

220 As shown by Hoppe et al. (this issue), both Chl-a data sets (Chl-a$_{HPLC}$ and Chl-a$_{FLUO}$) were very

221 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

222 used to derive primary production rates (see section 3.6).

223 *2.7 Phytoplankton size class analyses*

224 Three pigment-based phytoplankton size classes (micro-, nano-, and picophytoplankton) were

225 estimated following the procedure as in Uitz et al. (2009), using defined marker pigment

226 concentrations in relation to Chl-a$_{HPLC}$, which has been tested for the SO waters (e.g., Uitz et al.,

227 2009). Microphytoplankton corresponds to phytoplankton with size >20 μm, nanophytoplankton

228 between 2-20 μm, and picophytoplankton between 0.2-2 μm. Detailed description of the

229 calculation is presented in Cheah et al. (this issue).

230 *2.8 Zooplankton*

231 Zooplankton samples were collected from the upper 250 m of the water column during double

232 oblique tows using a Rectangular Midwater Trawl (RMT 1+8) equipped with 1 m^2 (0.33 mm mesh

233 size) and 8 m^2 (4.5 mm mesh size) nets. RMT8 samples were representative of the

234 macrozooplankton and RMT1 samples were representative of the mesozooplankton (Atkinson and

235 Peck, 1990; Ward, 1989). A flowmeter (Hydro Bios, Kiel) was mounted in the mouth of the

236 RMT8 to measure the water volume filtered. Net tows were conducted at a speed of 2 to 2.5 kn.

237 RMT8 samples were preserved in a 4% formaldehyde and seawater solution. Specimens were

238 identified to the species level, counted and measured. Dry weight biomass was calculated using

239 known length-weight relationships (Mizdalski, 1988; E. Pakhomov, *unpublished data*). RMT1

240 samples were split and one half preserved in a 4% formaldehyde and seawater solution formalin,

241 and the other half sieved, dried at 50°C for 48 hours, and weighed for sample dry weight.

242 **3. RESULTS**

243 *3.1 Hydrography: Fronts and water masses*

244 Vertical meridional potential temperature (θ), salinity, potential density, oxygen, DFe and Chl-

245 a_{FLUO} over the upper 500 m are shown in Figure 1. A detailed description of the hydrographic

246 characteristics encountered along the 10°E transect is given in Strass et al. (this issue). The Sub-

247 Antarctic Front (SAF), located at 46.5ºS, was identified by an abrupt southward decrease in

248 surface temperature and salinity. The Antarctic Polar Front (APF), apparent at 49.3ºS based on

249 density profiles, was also associated with the northernmost extent of the temperature minimum

250 layer. Finally, at 52.5ºS, the Southern Polar Front (SPF) was defined by a strong increase in

251 salinity and steep decrease in surface temperatures.

252 Also indicated in Figure 1 are the water masses sampled along the 10ºE transect (Strass et al., this

253 issue). Antarctic Surface Waters (AASW) and Sub-Antarctic Surface Waters (SASW) occupied

254 the upper ~100 m south of the SAF. Below the pycnocline, Antarctic Intermediate Water (AAIW),

255 with its salinity minimum of 34.2, extended northward of the SAF below depths of 300 to 400 m,

256 whereas Upper Circumpolar Deep Water (UCDW) (salinity = 34.75 and θ = 2ºC) was only found

257 south of the SPF. North of the SAF, a subsurface salinity maximum was evident between 100 and

258 300 m. This feature likely originated farther north where it was subsequently displaced southward

259 as an anticyclonic eddy (Strass et al., this issue). Previous observations of such subsurface lobes of

260 saltier water indicate that this is a common feature of the Subtropical Frontal Zone, located farther

261 north of this transect (Heath, 1976; Smythe-Wright et al., 1998). Poleward compensation of

262 Ekman convergence has been suggested as the origin of these features (Heath, 1976), which were

263 occasionally found as far south as 50ºS (Deacon, 1945).

264 *3.2 Dissolved iron*

265 DFe concentrations were generally low along the meridional transect, ranging from 0.08 to 0.33

266 nM in the upper 100 m and varied the major gradients of other ancillary parameters (Figure 1e and

267 Figure S1). Highest concentrations were measured in the upper 25 m of the SAZ (44ºS-46ºS)

268 decreasing southwards, with almost full depletion at ~50ºS. This corresponds to the area where the

269 highest Chl-a$_{FLUO}$ values were also found (Figure 1f). Indeed, Chl-a$_{FLUO}$ and DFe concentrations

270 were significantly inversely correlated (Spearman correlation coefficient, $\rho = -0.83$, $p < 0.0001$, n =

271 21).

272 A subsurface increase of DFe was observed at 40 m at the two southernmost stations (81 and 84)

273 as well as a layer (60-80 m) of depleted DFe (0.07-0.13 nM), that matched a deep Chl-a$_{FLUO}$

274 maximum (~0.6 mg m^{-3}) (Figure 1e and 1f). At these same stations below 100 m, higher

275 concentrations of DFe occurred, which were positively correlated with salinity and negatively

276 correlated with oxygen (Pearson correlation coefficient, $r = 0.82$ and $\rho = -0.85$, respectively, p

277 <0.01, n = 9). Furthermore, these high DFe concentrations were associated with the highest

278 concentrations of nitrate and phosphate measured along this section (>35 μM for nitrate and >2.4

279 μM for phosphate; data not shown). A subsurface maximum of DFe (80-200 m) was also observed

280 in the SAZ, coinciding with a subsurface salinity maximum (Figures 1b, 1e).

281 ### 3.3 ^{234}Th deficits and fluxes

282 Significant deficits of ^{234}Th relative to ^{238}U (up to ~45%) were found in the upper 100-200 m of

283 the water column at all the stations (Figure 2), with lowest deficiencies (~25%) observed at the

284 two southernmost stations (52ºS and 53ºS). Deficits were consistent with the primary production

285 zone (PPZ), here defined as the depth where fluorescence is reduced to 10% of its maximum value

286 (Owens et al., 2014; Table 1). No significant ^{234}Th excess was observed. At 300-350 m, an

287 additional small depletion of ^{234}Th was measured at the two southernmost stations. This depletion

288 was not considered when estimating fluxes at depth due to poor vertical resolution below 200 m.

289 Steady state water column ^{234}Th fluxes, derived from the integrated ^{234}Th deficits with respect to

290 ^{238}U activities, were determined at three depths at each station (Table 3; Figure 3): i) the

291 equilibrium depth (Eq. depth; i.e., first depth where there is no significant difference between ^{238}U

292 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 52°S

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 46°S and 50°S (see section 3.5) we

323   used C/^{234}Th and N/^{234}Th ratios measured at stations at 44°S and 52°S, which belonged to the

324   same biogeochemical provinces, respectively (44°S and 46°S: SAZ; 50°S and 52°S 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 44°S to 48°S, 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^{-}

378 ^{1}) are within the mid to upper range of previously reported estimates (from negligible to 3800 dpm

379 m^{-2} d^{-1}; on average 1660 ± 920 dpm m^{-2} d^{-1}, n = 201; Figure 4). Our Th-derived POC fluxes

380 estimated along the 10ºE transect (25 to 41 mmol C m^{-2} d^{-1}) are, however, among the highest

381 fluxes reported to date within the SO (from negligible to 91 mmol C m^{-2} d^{-1}; on average 13 ± 13

382 mmol C m^{-2} d^{-1}; n = 273; Figure 4; also see compilations by Maiti et al., 2013 and Le Moigne et

383 al., 2013), and close to values found in areas with natural and artificially high iron inputs (e.g.,

384 Morris et al., 2007; Smetacek et al., 2012). This is surprising given that our measurements were

385 conducted in open ocean areas of the ACC. In the following sections, the effects of physical

386 processes are investigated in order to validate the 1-D steady state approach applied (section 4.1).

387 The distribution of DFe is discussed relative to previous studies and with ^{234}Th activity profiles.

388 Biological uptake and possible inputs linked to water masses are also explored (section 4.2).

389 Variability in export along the transect is also examined in light of planktonic community

390 structure in order to provide insight into the main drivers of POC export fluxes throughout the

391 region (section 4.3), and how differences in food webs may affect POC export and transfer

392 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).

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 $< 20\%$.

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

417   (Sokolov and Rintoul, 2007). DFe concentrations in the Atlantic sector of the ACC progressively

418   decrease eastwards as the ACC moves from the main iron source (the Antarctic Peninsula and

419   South Georgia, de Jong et al., 2012). Despite the high spatial variability shown here, our DFe data

420   are in excellent agreement with the few prior sampling efforts carried out in this sector of the SO

421   (Figure S1) (Chever et al., 2010; Klunder et al., 2011) suggesting that major features in DFe

422   distributions are persistent during the austral summer.

423   Satellite images show high Chl-a concentrations (up to 1.3 mg m^{-3}) north of the APF about a

424   month prior to the cruise (Figure 5; Figure S2). However, DFe concentrations in that area were not

425   as depleted as in the central region of the transect during the cruise (Figure 1e). The biological

426   uptake of DFe north of the APF might have been limited by silicate availability since silicate

427   concentrations were in the range of limiting concentratrions, namely ≤ 1 μM (Figure 7) (Le

428   Moigne et al., 2013a, Cheah et al., this issue). Additionally, the high salinity intrusion at 100-300

429   m supports a lateral advection of DFe (Figures 1b and 1e). During the cruise, the highest Chl-a

430   concentrations (up to 1.2 mg m^{-3}; Figure S1) were measured between 49ºS and 52ºS (Figure 5e),

431   leading to strong depletion of DFe in the upper 100 m. The low DFe values were probably caused

432   by recent biological uptake and the subsequent removal through sinking particles. Biological

433   uptake of DFe would explain its inverse correlation with Chl-a$_{FLUO}$ ($\rho = -0.83$, $p < 0.0001$, n = 21).

434   In general, DFe and ^{234}Th/^{238}U profiles followed a similar trend with depth, and are inverse to Chl-

435   a$_{FLUO}$ profiles, with DFe depletion matching the increase of ^{234}Th deficits (Figure S1). This

436   suggests that the process causing the reduction of DFe concentrations also affected the ^{234}Th

437   deficits at a similar depth range. However, it should be noted that the gradient in ^{234}Th deficits are

438   steeper than gradients in DFe (between ~60 - 200 m), probably due to a more rapid turnover of Fe

439   than that of ^{234}Th, a finding also reported by Klunder et al. (2011).

440   The highest DFe concentrations were found in the southern part of the transect (St. 81 and 84),

441   below ~300 m associated with UCDW waters, where oxygen concentrations were (<200 μmol kg^{-}

442 [1]) (Figure 1d). Indeed, DFe concentrations below 100 m were strongly correlated with salinity and

443 negatively correlated with oxygen at those two stations ($\rho = 0.88$ for salinity and $\rho = -0.85$ for

444 oxygen, with $p < 0.01$ and n = 9 for both correlations). Higher DFe concentrations have been

445 found previously in UCDW waters (Klunder et al., 2011) and are typical of reduced oxygen

446 concentrations due to an increase of iron solubilization during POC remineralization and

447 stabilization of highly soluble Fe(II) (Millero et al., 1987). Low Chl-a$_{FLUO}$ values despite high

448 concentrations of all major nutrients at the southern end of the transect (Figure 7) indicate,

449 however, that little of the DFe in UCDW waters reaches the photic layer.

450 **4.3 Differences in planktonic community N-S of the APF: Effects on POC export and**

451 **attenuation**

452 SO fronts are physical boundaries that delimit zones of distinct physical, chemical, and biological

453 properties (e.g., Read et al., 2002; Strass et al., 2002b) that in turn could regulate the particle

454 export flux. In this study we did not observe a clear zonation related to the fronts regarding [234]Th

455 export fluxes, although enhanced export was measured in areas where, as indicated by satellite

456 imagery (Figure 5, Figure S2), phytoplankton blooms occurred and peaked about a month prior to

457 our sampling (north of the APF). Since the [234]Th method integrates over time scales of several

458 weeks, we could expect a decoupling between [234]Th deficiencies in the upper water column as

459 compared to the biological parameters measured during the cruise (e.g., Chl-a concentrations or

460 primary production) (Buesseler, 1998).

461 The POC export fluxes at 100 m were in the higher end of the range of previous reported

462 estimates, mainly driven by high C/[234]Th ratios (Figure 4). Further, contrary to [234]Th fluxes, POC

463 fluxes were not correlated with latitude ($r^2 = 0.27$; $p = 0.29$; similar for PON fluxes: $r^2 = 0.08$; $p =$

464 0.59) (Figure 3). Differences between stations north and south of the APF were found when

465 comparing changes in POC export fluxes at 100 and 400 m. Due to changes in C/[234]Th ratios with

466 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 μ mol 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

569   APF were lower (max. 44%). A relatively small export efficiency (27%) was also confirmed south

570   of the APF using sediment trap results deployed at 53ºS (MH. Iversen, *pers. comm.*).

571   Stations south of the APF, however, had the highest transfer efficiencies (i.e., the percentage of

572   POC flux at the equilibrium depth that reaches 400 m), ranging between 89% and 148% (Table 3).

573   As discussed previously, these high transfer efficiencies can be explained by fast-sinking and

574   weakly attenuated sinking material, combined with the effect of diel vertical migration of

575   zooplankton (Cavan et al., 2015). Alternatively, these high transfer efficiency might be due to an

576   overestimate of our $C/^{234}Th$ ratios based on particles >53 μm (not necessarily sinking particles).

577   Differences in attenuation are, however, primarily due to the fact that, in strong contrast to stations

578   north of the APF, $C/^{234}Th$ ratios south of the APF do not change with depth. $C/^{234}Th$ ratios in

579   sediment trap material (measured only at 53ºS), although lower than the ratios obtained from ISP,

580   also present no decrease with depth. A comparison of $C/^{234}Th$ ratios from several trap

581   deployments south of the APF during the same cruise (Roca-Martí et al., this issue) did not show a

582   systematic bias for $C/^{234}Th$ ratios for ISP collected material compared to trap collected material.

583   Further, no large differences were observed in $C/^{234}Th$ ratios between 100 m and 300 m, similar to

584   our results. In Roca-Martí et al. (this issue), Chl-a and fucoxanthin were found to be efficiently

585   transferred between 100 and 300 m indicating that these pigments were exported to 300 m with

586   little to no breakdown. Results from Cedhagen et al. (2014), obtained during the same expedition,

587   also corroborate these findings as large concentrations of algal pigments were observed in the

588   cytoplasm of foraminifera collected at depths >4000 m. Moreover, at station 81 (52ºS; ~3500 m

589   depth), Ruff et al. (2014) observed a large number of diatom frustules and intact fecal pellets in

590   the top layers of the sediments, even down to 5 cm depth. Combined these studies suggest rapid

591   transport of material to sediments using a variety of pathways.

592   *4.5 Comparison with previous studies*

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

594 in http://doi.pangaea.de/10.1594/PANGAEA.809717, contains a number of studies located in the

595 SO (iron fertilization experiments not included). Considering all these studies together with the

596 results from our expedition presented here and in Roca-Martí et al. (this issue), as well as

597 Planchon et al. (2015), Rosengard et al. (2015) and Savoye et al. (2008), we observed wide ranges

598 in ^{234}Th export fluxes and C/^{234}Th ratios, with subsequent variability in the derived POC fluxes at

599 100 ± 10 m depth (Figure 4). This compilation, however, includes a variety of areas that are

600 difficult to compare with our open ocean stations due to the large differences in phytoplankton

601 assemblage and growth and biogeochemical aspects linked to their geographical location (e.g., ice

602 coverage or Fe inputs from continental shelves). Therefore, here we only discuss our results

603 together with studies conducted in the Atlantic sector of the open ACC (between 40ºS-60ºS and

604 15ºE-15ºW; see map inset in Figure 4) namely Planchon et al. (2013), Roca-Martí et al. (this

605 issue), Rutgers van der Loeff et al. (2011, 2002, 1997) and Smetacek et al. (2012), outside the iron

606 fertilization patch.

607 Except for the SO-JGOFS expedition (Rutgers van der Loeff et al., 1997), which was conducted

608 during the austral spring (Oct-Nov 1992; 6ºE), all the studies discussed here were conducted

609 during the austral summer (Dec-Jan) or late austral summer (Feb-Mar). During the austral spring,

610 short but intense bloom events seem to contribute significantly to the annual C export. Data in

611 Rutgers van der Loeff et al. (1997) supports this observation with a maximum ^{234}Th export flux of

612 3250 dpm m^{-2} d^{-1} at 100 m during a productive period of only 22 days and a POC flux at 100 m

613 ranging from 19 to 38 mmol C m^{-2} d^{-1}, similar to the results observed during our study. Rutgers

614 van der Loeff et al. (2002) reported constant export fluxes during a two week period of the austral

615 summer three years later (1995/96). ^{234}Th and POC export fluxes at 100 m were 865 dpm m^{-2} d^{-1}

616 and 8.8 mmol C m^{-2} d^{-1}, respectively. The magnitude of the fluxes presented by Rutgers van der

617 Loeff et al. (2002) is similar to those reported by Planchon et al. (2013) during the Bonus

618 GoodHope (BGH) expedition (Feb-Mar 2008), ranging from 870 to 1200 dpm m^{-2} d^{-1} and 2.3 to

619 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.

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