| 1 | Rapid acidification of mode and intermediate waters in the southwest Atlantic |
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| 25 | Abstract |
| 26 | Observations along the southwest Atlantic WOCE A17 line made during the Dutch |
| 27 | GEOTRACES-NL program (2010-11) were compared with historical data from 1994 to |
| 28 | quantify the changes in the anthropogenic component of the total pool of dissolved inorganic |

29 carbon (ΔC_{ant}). Application of the extended Multi Linear Regression (eMLR) method shows that the ΔC_{ant} from 1994 to 2011 has largely remained confined to the upper 1000 dbar. The 30 greatest changes occur in the upper 200 dbar in the SubAntarctic Zone (SAZ), where a 31 maximum increase of 37 µmol kg⁻¹ is found. South Atlantic Central Water (SACW) 32 experienced the highest rate of increase in C_{ant} , at 0.99±0.14 µmol kg⁻¹ y⁻¹, resulting in a 33 maximum rate of decrease in pH of 0.0016 yr⁻¹. The highest rates of acidification relative to 34 ΔC_{ant}, however, were found in SubAntarctic Mode Water (SAMW) and Antarctic 35 Intermediate Water (AAIW). The low buffering capacity of SAMW and AAIW combined 36 with their relatively high rates of C_{ant} increase of 0.53 \pm 0.11 $\mu mol~kg^{\text{--}1}~y^{\text{--}1}$ and 0.36 \pm 0.06 37 umol kg⁻¹ y⁻¹, respectively, has lead to rapid acidification in the SAZ, and will continue to do 38 so whilst simultaneously reducing the chemical buffering capacity of this significant CO₂ 39 40 sink.

41

42 1 Introduction

43 The Atlantic Ocean contains the largest store of anthropogenic carbon (C_{ant}) of all the world's 44 oceans, accounting for approximately 38% of the total Cant inventory (Sabine et al., 2004). 45 Within the Atlantic, the North Atlantic has been found to be responsible for the majority of 46 the uptake of C_{ant}, due to the formation of North Atlantic Deep Water (NADW)(Lee et al., 47 2003; Sabine et al., 2004). However, a recent Atlantic basin inventory analysis indicates that in the past decade the South Atlantic has been more effective at sequestering Cant 48 (Wanninkhof et al., 2010) than the North Atlantic. These authors calculated a rate of increase 49 of the North Atlantic inventory of 1.9 Pg C decade⁻¹, whereas the South Atlantic inventory 50 grew at a rate of 3.0 Pg C decade⁻¹. Calculations by Ríos et al. (2012) indicate that the 51 52 southwestern Atlantic Ocean dominates the South Atlantic sink of Cant, with a storage rate of 0.25±0.035 Pg C decade⁻¹. Quantifying the exact rate of increase in anthropogenic carbon in 53 54 ocean waters is inherently problematic due to the highly variable nature of DIC within the 55 ocean and the relatively small fraction of total dissolved inorganic carbon (DIC) that the 56 anthropogenic component represents (~3%; Ríos et al., 2010). In the past decade a number of methods for calculating the increase in C_{ant} (ΔC_{ant}) between reoccupation of ocean transects 57 have been developed (TrOCA, φC_T^{0} , eMLR). Despite the differing approaches and 58 59 assumptions, there is overall coherence in the determinations of the anthropogenic

component of inorganic carbon in the Atlantic Ocean (Lee et al., 2003; Vázquez-Rodríguez et
al., 2009a; Peng et al., 2010; Wanninkhof et al., 2010).

62

The southwest Atlantic has been occupied several times over the past 20 years and several 63 techniques to determine C_{ant} have been applied to the WOCE '94 A17 transect by Ríos et al. 64 65 (2010). These methods included ΔC^* (Gruber et al., 1996), Tracer combining Oxygen, 66 inorganic Carbon and total Alkalinity (TrOCA)(Touratier et al., 2007), ϕ CT° (Vázquez-Rodríguez et al., 2009a), and Transit Time Distributions (TTD)(Waugh et al., 2006) and 67 showed general conformity in the distribution of C_{ant}. The presence of the western boundary 68 current in the South Atlantic Ocean means that the Cant signal penetrates deeper and is larger 69 70 in the western half of the basin compared to the eastern half (Wanninkhof et al., 2010; Ríos 71 et al., 2010; Vázquez-Rodríguez et al., 2009a). Similarly, Murata et al. (2008) show that the C_{ant} signal in SubAntarctic Mode Water (SAMW) can be ~7 µmol kg⁻¹ higher west of 15°W 72 compared to the east. Mode and intermediate water formation constitute a major pathway of 73 74 Cant into the South Atlantic Ocean interior (McNeil et al., 2001; Sabine et al., 2004). The 75 SAMW is formed in the Subantarctic Zone (SAZ), between the Subtropical Front (STF) and subAntarctic Front (SAF), where a calculated anthropogenic CO_2 uptake of 0.07 - 0.08 PgC 76 yr⁻¹ occurs (Sabine et al., 1999; McNeil et al., 2001). A total CO₂ sink of 1.1 Pg C yr⁻¹ has 77 been calculated by McNeil et al. (2007) for the SAZ, making it the largest CO₂ sink in the 78 79 Southern Ocean and a significant sink for anthropogenic atmospheric CO₂.

80

81 The increase in DIC that results from the uptake of anthropogenic CO_2 from the atmosphere 82 leads to increasing proton, bicarbonate ion and carbon dioxide concentrations ([H⁺], [HCO₃⁻ 83],[CO₂]) and decreasing carbonate concentrations ([CO₃²⁻]), a process referred to as *ocean*

84 *acidification*. Sabine et al. (2004) state that approximately 50% of the total amount of C_{ant} in

the world's oceans resides in the upper 400 m. The associated decrease in pH has been

86 calculated as 0.1 pH units in the surface ocean relative to pre-industrial times (Orr et al.,

2005) and is ongoing. Observations have found acidification rates of 0.0016 ± 0.0001 yr⁻¹ and

 $0.0012\pm0.002 \text{ yr}^{-1}$, in the North Atlantic Ocean, for Subarctic Intermediate Water (SAIW)

and SubPolar Mode Water (SPMW), respectively (Vázquez-Rodríguez et al., 2012). Data

90 from the European Time Series in the Canary Islands (ESTOC) station shows significantly

91 higher rates of pH decrease in surface waters of 0.0017 ± 0.0004 yr⁻¹, for the time period

92 1995 to 2004 with notable influence from regional climatic forcing (Santana-Casiano et al.,

- 93 2007). Acidification rates that deviate from the rate that is expected from C_{ant} increases alone
- 94 have been observed in upper Labrador Sea Water (uLSW), SAIW, and eastern North Atlantic
- 95 Central Water (eNACW) (Vázquez-Rodríguez et al., 2012). These variations have been
- 96 attributed to a combination of climatic and biological effects. The greater sensitivity of some
- 97 water masses to acidification has been well documented by González-Dávila et al. (2011)
- 98 through the application of the buffering factors described by Egleston et al. (2010). González-
- 99 Dávila et al. (2011) highlighted waters originating at high latitudes as particularly sensitive to
- 100 increases in the concentration of dissolved CO_2 ([$CO_2(aq)$]), in particular Antarctic
- 101 Intermediate Water (AAIW) and upper Circumpolar Deep Water (*u*CDW) due to low total
- 102 alkalinity (A_T) to DIC ratios.
- 103

104 A number of the biological consequences of ocean acidification are related to the changes in 105 carbonate, and thus calcium carbonate (CaCO₃), ion concentration. Carbonate ions are used 106 by marine calcifying organisms to form both varieties of calcium carbonate: aragonite (e.g. 107 by pteropods) and calcite (e.g. by coccolithophores and foraminifera). Aragonite is the less 108 metastable form of CaCO₃ resulting in a saturation horizon ($\Omega_{Ar}=1$) approximately 2 km 109 shallower than that of calcite in the South Atlantic Ocean, below which depth the CaCO₃ 110 present will be in dissolved form. A number of experiments have observed shell dissolution 111 in pteropods incubated at elevated partial pressure of CO_2 (pCO₂) (Orr et al., 2005; Lischka et 112 al., 2011) associated with a lowering of the aragonite saturation state. Recently similar results 113 have been observed in situ in the Southern Ocean (Bednaršek et al., 2012), indicating that species are already being affected by C_{ant} accumulation. Organisms that use aragonite are 114 thus much more vulnerable to decreases in $[CO_3^{2-}]$ driven from the surface increase in $[CO_2]$ 115 116

- 117 This study examines the increase of C_{ant} in the southwest Atlantic Ocean between two
- 118 occupations of the WOCE A17 line, which took place in 1994 and 2010/11. We calculate the
- 119 changes in C_{ant} (ΔC_{ant}) in the different water masses and subsequently examine the pH
- 120 changes driven by the invasion of anthropogenic carbon between WOCE '94 A17 and
- 121 GEOTRACES-NL (2010/2011). These results are furthermore put into context with regard to
- 122 the differing buffering capacities of individual water masses.

124 **2 Data**

- 125 The two datasets used in this study are the results from the CO₂ survey data from the WOCE
- 126 '94 A17 section (public data at: http://cdiac.ornl.gov/oceans/woce_a17c.html) and the Dutch
- 127 West Atlantic GEOTRACES program, completed in 2011 (GEOTRACES-NL
- 128 (2010/2011)(public data available at: http://www.bodc.ac.uk/geotraces/data/idp2014/). The
- respective stations from the two campaigns are shown in Fig. 1. The GEOTRACES-NL
- 130 (2010/2011) section was carried out in two parts. The shown stations north of the equator
- 131 were occupied in July 2010 by the Dutch RV Pelagia (expedition 64PE321, from Hamilton,
- 132 Bermuda to Fortaleza, Brazil), and the southern hemisphere was sampled during March 2011
- by the British RRS James Cook (JC057, from Punta Arenas, Chile to Las Palmas, Gran
- 134 Canaria).
- 135

136 2.1 WOCE '94 A17 measurements

- 137 The WOCE '94 A17 section was similarly carried out in austral autumn and this data has
- 138 undergone rigorous quality control (Key et al., 2010). The data report is available from
- 139 'http://cdiac.ornl.gov/oceans/ndp_084/' (Ríos et al., 2005), where an offset of -8 μ mol kg⁻¹ in
- 140 the total alkalinity (A_T) data has been reported and corrected for in this study. From this
- 141 dataset only the stations where data for both A_T and DIC are available, were used. This
- resulted in a total of 59 stations and 1683 datapoints. For a detailed analysis of the WOCE
- 143 occupation we refer the reader to Ríos et al., (2010).
- 144

145 2.2 GEOTRACES-NL (2010/11) measurements

146 **2.2.1 Dissolved inorganic carbon and total alkalinity**

- 147 During the GEOTRACES-NL (2010/2011) cruises, for measurements of DIC and A_T, water
- samples of 600 ml were collected from throughout the water column, from 24 Niskin
- samplers mounted onto a CTD rosette, following standard operating procedures (Dickson et
- al., 2007). At least two duplicates samples were collected at each station, from different parts
- 151 of the profile. Samples were analyzed immediately after collection on a VINDTA 3C
- 152 (Versatile INstrument for the Determination of Total Alkalinity, Marianda, Kiel) instruments,
- simultaneously. This system determines DIC by coulometric titration using a coulometer

- 154 (Johnson et al., 1987) and determines A_T by potentiometric titration with 0.1M hydrochloric
- acid (Mintrop et al., 2000). Quality control was performed through regular measurements of
- 156 certified reference material (CRM, Batch #100) supplied by Dr. Andrew Dickson at Scripps
- 157 Institute of Oceanography (San Diego, California). Based on the measurements performed on
- 158 the CRM throughout both cruises, DIC was measured with a precision of $\pm 1.0 \,\mu$ mol kg⁻¹ and
- 159 the precision of A_T was $\pm 1.1 \ \mu mol \ kg^{-1}$.
- 160

161 **2.2.2 Ancillary parameters**

- 162 Dissolved oxygen samples were collected from a minimum of three depths throughout the
- 163 water column for CTD sensor calibration. Inorganic nutrients (PO₄, Si(OH)₄, NO₃) were
- analyzed following the methods of Grasshoff et al. (1983). In every run a control and a
- 165 natural sterilized, Reference Nutrient Sample (RMNS Kanso, Japan) were measured for
- 166 validation. Precision was estimated to be \pm 0.01, 0.2, and 0.2 µmol l⁻¹ for PO₄, Si(OH)₄, and
- 167 NO₃, respectively. Values of salinity are reported on the practical salinity scale.
- 168

169 2.2.3 pH Calculations

- 170 From DIC, A_T and supplementary data (salinity, temperature, pressure, Si(OH)₄, PO₄), the pH
- and pCO₂ were also calculated in-situ for both datasets using CO2_SYS (Lewis and Wallace,
- 172 1998) adapted for Matlab (van Heuven, 2011a), applying the acid dissociation constants of
- 173 Mehrbach et al. (1973, refit by Dickson and Millero, 1987), and the KSO₄ constant of
- 174 Dickson (1990). Identical calculation were carried out on A_T and DIC data from both the
- 175 WOCE '94 A17 and GEOTRACES-NL (2010/2011) datasets, with the resulting pH reported
- 176 on the total pH scale.
- 177

178 **2.3** Consistency between datasets

- 179 In a later section, we employ the extended Multi Linear Regression (eMLR) method
- 180 (Wallace, 1995; Friis et al., 2005) to infer ΔC_{ant} between the two cruises. The eMLR method
- 181 considers various biogeochemical properties (in this case, salinity, DIC, NO₃, Si(OH)₄ and
- apparent oxygen utilization (AOU= $[O_2]_{sat}$ - $[O_2]_{obs}$)) and is particularly sensitive to large scale
- 183 ('secular') changes in the distributions of these properties, as well as to analytical biases in
- their measurement. In order to assess the magnitude and distributions of these changes, we
- 185 gridded the values of salinity, DIC, NO₃, Si(OH)₄ and AOU of each dataset and the gridded

186 WOCE dataset was subtracted from the GEOTRACES grid. Grid spacing was every 2

187 degrees of latitude, with 80 layers in the vertical direction, with increased density towards the

188 surface. In the *lower* Circumpolar Deep Water (*l*CDW; conceivably the most stable water

mass in the section) the differences average -0.01 ± 0.015 (salinity), -4.2 ± 12.1 µmol kg⁻¹

190 (DIC), -1.92±0.78 μmol kg⁻¹ (NO₃), -5.05±3.3 μmol kg⁻¹ (Si(OH)₄) and -3.13±3.9 μmol kg⁻¹

- 191 (AOU).
- 192

193 By limiting the comparison to just *l*CDW the number of data points available is limited, as

such, we further performed a more robust crossover analysis of the GEOTRACES 2010/11

dataset with data from the CARINA database (CARINA Group, 2009; Tanhua, 2010). This

196 was done for all the used tracers at depths deeper than 3000m. We find an offset of $+1\pm0.8\%$

197 for NO₃, $-1\pm0.5\%$ for dissolved oxygen, -0.004 ± 0.001 for salinity, $-1\pm0.3\%$ for Si(OH)₄,

198 $+1.17\pm2.8 \ \mu\text{mol kg}^{-1}$ for DIC, and $+5.3\pm4.4 \ \mu\text{mol kg}^{-1}$ for A_T. These values are all within the

- threshold values of the CARINA synthesis (Key et al., 2010) thus no corrections wereapplied to our data.
- 201

202 **3** Methods

203 3.1 eMLR and Cant Calculations

204 There are two general carbon data-based approaches for studying the increasing oceanic C_{ant}. 205 The first approach uses back-calculation techniques to obtain an estimate of pre-industrial 206 DIC concentration against which to compare current measurements. Methods from the 207 second approach aim to determine the part of change in DIC between two specific time 208 periods that is attributable to anthropogenic invasion. One example of each approach is 209 employed in this study; eMLR (Friis et al., 2005) and φC_T (Vázquez-Rodríguez et al., 2009a, 210 2009b). Various comparison and evaluations of these and other methods are available in the 211 literature (Levine et al., 2008; Yool et al., 2010; van Heuven et al., 2011b; Sabine and 212 Tanhua, 2010).

213

214 **3.1.1** ΔC_{ant} from eMLR

215 The multi-linear regression approach to estimating anthropogenic CO₂ invasion was

216 introduced by Wallace (1995). It involves using a number of biogeochemical properties,

known to be related to DIC, to obtain a model of the observed DIC. As the relationships

between DIC and these properties are expected not to change over time, the same statistical relationships can be applied to a second dataset of later date. Differences between the thus 'predicted' DIC and the observed DIC are attributed to the invasion of anthropogenic CO_2 . In the extended version (eMLR) developed by Friis et al. (2005), which is applied here, the DIC from two datasets is fitted to the same selection of properties from both datasets, and the difference between parameter coefficients is assumed to be predictive of the difference in C_{ant} between the two cruises:

227

 $\Delta C_{ant}^{eMLR} = DIC^{MLR2,t2} - DIC^{MLR1,t1}$ (1) = $(a_2 - a_1) + (b_2 - b_1) SiO_{2t2} + (c_2 - c_1) NO_{3t2} + (d_2 - d_1) AOU_{t2} + (e_2 - e_1)$ $S_{t2} + (f_2 - f_1) T_{t2} + (g_2 - g_1) P_{t2}$ (2)

Following equation 2, we apply the backward calculation technique as the DIC data from the more recent GEOTRACES-NL (2010/2011) cruise demonstrates a greater precision. The properties used to predict DIC in the WOCE '94 dataset results in an R² value of 0.97 and a root mean square error (rmse) of 10.7 μ mol kg⁻¹. For the GEOTRACES-NL (2010/2011) dataset a R² of 0.98 was obtained and a rmse of 9.9 μ mol kg⁻¹ (Fig. 2).

233

234 The eMLR regressions were applied along isopycnals intervals, as the preferred method of 235 water movement from the surface into the ocean interior is along surfaces of constant density. 236 It thus follows that waters occupying the same density band share a common formation 237 history and can be described by a single equation. Isopycnal bands were chosen based on 238 temperature-salinity plots of the water masses and the amount of data occupying each 239 interval. The coefficients and accompanying statistics from each isopycnal interval are 240 displayed in Table 1(a) and (b) for the 1994 and 2010/11 regressions, respectively. The residuals of each fit are shown in Fig. 2, with the 2011 dataset showing an average of 2.1 241 µmol kg⁻¹ in the more stable deeper waters (>2000 dbar). In comparison, the WOCE '94 A17 242 dataset shows a deep water (>2000 dbar) column average residual of $3.17 \mu mol kg^{-1}$, which 243 244 we attribute to less precise measurements in the earlier dataset. Pressure was included in the 245 regression to avoid skewing (over depth) of the residuals of the MLR by the relatively large 246 amount of samples located towards the surface, as mentioned by Hauck et al. (2010). 247

248 **3.1.2** C_{ant} from ϕC_T°

249 The ϕC_T° method is a back-calculation approach that uses stoichiometric ratios from

- 250 biogeochemical processes to account for the addition of DIC in the water column resulting
- 251 from organic matter remineralization and calcium carbonate dissolution, since the time of
- water formation (Vázquez-Rodríguez, 2008; Vázquez-Rodríguez et al. 2009a). It is based on
- 253 the general principle of 'preformed DIC' (or C_T°) of Brewer (1978) and ΔC^* of Gruber et al.
- (1996). The main advantage of this method is that it considers the non-steady state of A_T and
- 255 pCO₂ in the subsurface reference layer.
- 256

257 3.2 Buffer Factors

258 The revelle factor was originally described by Revelle and Suess (1957) and quantified the 259 attenuated response of increasing DIC impacted by increasing pCO_2 , or vice versa. This work 260 has been built upon by Egleston et al. (2010), who outlined six expressions that define how $[CO_2]$, $[H^+]$, and Ω_{Ar} or Ω_{Ca} , are impacted by changes in DIC or A_T . The following three 261 262 expressions for the buffer factors relating to DIC were applied to the GEOTRACES-NL (2010/2011) and WOCE '94 A17 southwest Atlantic sections (Equations (3-4) and (6-7) are 263 264 taken from Egleston et al., (2010), however, Equation (5) and (8) are taken from Álvarez et al., (2014), who identified and corrected a typo in the definitions of Egleston et al., 2010). 265 $\gamma DIC = DIC - Alk_{C}^{2}/S,$ 266 (3) $\beta DIC = DIC \times S - Alk_{C}^{2}/Alk_{C}$ 267 (4) $\omega DIC = DIC - \{Alk_C \times (2 \times [CO_2] + [HCO_3])/P\},\$ 268 (5) $DIC = [CO_2] + [HCO_3] + [CO_3^2],$ 269 where (6) $Alk_{C} = [HCO_{3}^{-}] + 2[CO_{3}^{2-}],$ 270 (7) $P = [HCO_3^{-}] - \{[H^+][B(OH)_4^{-}]/Khb + [H^+]\} - [H^+] + [OH^-],$ 271 (8) $S = [HCO_3^{-}] + 4[CO_3^{2-}] + [H^+] + [OH^-] + \{[H^+][B(OH)_4^{-}]/Khb + [H^+]\}(9)$ 272 and Ω refers to the saturation state of sea water with respect to aragonite or calcite. These 273 equations quantify the resistance to change of $[CO^2]$ (yDIC), $[H^+](\beta DIC)$ and $\Omega(\omega DIC)$ in a 274 275 water mass to changes in DIC. The concentrations used for the calculations were obtained 276 from CO2SYS (Lewis and Wallace, 1998, adapted for Matlab by van Heuven, 2011a) using 277 the same input conditions as previously mentioned (Sect. 2.2.3). 278

279 4 Hydrography of the South Atlantic Ocean

The distributions of potential temperature, salinity, AOU, silicate, A_T, and DIC of the 280 281 GEOTRACES-NL (2010/2011) section are shown in Fig. 3. The large water masses have 282 been described elsewhere (Mémery et al., 2000; Ríos et al., 2010; Wanninkhof et al., 2010), 283 thus here the treatment is relatively concise. Located deeper than 4500 dbar throughout the 284 section is Antarctic Bottom Water (AABW), characteristic in its high DIC and AOU. Values for DIC in this water mass range from 2243 to 2267 µmol kg⁻¹, and AOU values occupy a 285 narrow band between 111 to 128 µmol kg⁻¹. The DIC maximum (2267 µmol kg⁻¹) and 286 potential temperature minimum (-0.16°C) are both found in this water mass, which also 287 shows the deep water (>1000 dbar) A_T maximum (2369 µmol kg⁻¹). These characteristics are 288 289 all representative of the old age of the water mass and are caused by the large amount of 290 organic matter remineralization which has taken place within it. The AABW can, most easily, 291 be distinguished from the overlying *lower* Circumpolar Deep Water (*l*CDW), by the high silicate concentrations, which reach values greater than 120 umol kg⁻¹ in AABW. Silicate 292 293 concentrations in the deep waters (>4000 dbar) demonstrate a strong covariance with A_T 294 $(R^2=0.95)$, which has been previously noted and stems from the simultaneous dissolution of 295 opaline and calcium carbonate shells from the hard tissue of organisms (Pérez et al., 2002).

296

297 The *l*CDW has a core at approximately 3500 dbar at 50°S, above which it merges into *upper* 298 Circumpolar Deep Water (*u*CDW), with its respective core identified by an oxygen minimum 299 at approximately 1500 m (Mémery et al., 2000). Both branches of CDW display properties 300 similar to that of AABW, as they represent a mixture of AABW and Weddell Sea Deep 301 Water (Wong et al., 1999; Orsi et al., 1999). The uCDW and lCDW share isopycnals with 302 upper North Atlantic Deep Water (uNADW) and lower North Atlantic Deep Water 303 (*I*NADW), respectively, in the northern half of the section (Fig. 3a). The *u*CDW and 304 *u*NADW, occupy the density band between $\sigma_s > 27.4$ and $\sigma_3 < 41.47$, with the front between the 305 two water masses found at approximately 26°N (Mémery et al., 2000). The NADW has been 306 more recently ventilated than CDW and is thus distinguished by lower AOU values of ~60 µmol kg⁻¹ and DIC values lower than 2200 µmol kg⁻¹. The deeper *l*NADW can be separated 307 from *u*NADW through higher silicate values, which rise to 40 μ mol kg⁻¹, whereas *u*NADW 308 has maximum silicate concentrations of 20 µmol kg⁻¹ (Fig. 3d). The A_T values are also lower 309 (~20 μ mol kg⁻¹) in *u*NADW compared to *l*NADW. 310

312 The Antarctic Intermediate Water (AAIW) enters the section at 200 dbar just south of 48°S, identifiable as a tongue of water with very low salinity and A_T (34.05 and 2275 µmol kg⁻¹, 313 314 respectively)(Fig. 3b). The AAIW lies above *u*CDW and below SubAntarctic Mode Water 315 (SAMW) (Peterson and Whitworth, 1989). This water mass is carried northward at 316 intermediate depths between $\sigma_{\theta} > 27.1$ and $\sigma_{\theta} < 27.4$ (Ríos et al., 2012) from south of the SAF. 317 In the southwestern Atlantic Ocean AAIW extends further north than in other oceans, due to the western boundary current along the coast of South America (Talley, 1996). The AAIW is 318 319 a relatively young water mass and has AOU values comparable to NADW ($\sim 50 - 100 \mu$ mol 320 kg^{-1}), however, it can be distinguished from *u*NADW, in its northward reaches, by its 321 elevated silicate concentrations. Situated above the AAIW, the SAMW is often considered a 322 component of the AAIW (McCartney, 1977). This water mass can be easily identified by the tracer Si^{*} = $[Si(OH)_4]$ - $[NO_3]$ which has values from -10 to -15 µmol kg⁻¹ in regions of 323 324 SAMW formation (Sarmiento et al., 2004). The SAMW formation region is located just 325 south of 47°S in the Subantarctic Zone (SAZ), north of the SAF (McCartney, 1977) where 326 deep winter mixing forms this high-oxygen water mass.

327

328 We locate the Subtropical Front (STF) at ~41°S, where there is a steep gradient in salinity in 329 the surface 200 dbar. North of the STF, in the surface, and extending northward to a density of σ_{0} <26.5 kg m⁻³, is South Atlantic Central Water (SACW; Ríos et al., 2012), heavily 330 depleted in silicate, and with elevated salinity and A_T. Against this background, the two 331 332 Amazon plumes are very distinct at 5°N and 15°N with salinity and A_T values as low as 34.11 and 2265 μ mol kg⁻¹, and 32.3 and 2157 μ mol kg⁻¹, respectively. The maximum values 333 334 of both salinity and A_T correspond with South Atlantic Central Water (SACW) in the subtropics (17°S), reaching absolute maxima of 37.5 and 2456 µmol kg⁻¹, respectively, at 50 335 336 dbar depth. The subtropical part of the SACW that features high salinity and A_T is often 337 referred to as the Salinity Maximum Water (SMW). In this study we make no distinction 338 between SMW and SACW.

339

340 5 Results and discussion

341 5.1 Anthropogenic carbon in the southwest Atlantic Ocean

342 The distribution of C_{ant} in 2011, calculated using the φC_T° method (Vázquez-Rodríguez, 2008; Vázquez-Rodríguez et al. 2009a), and the calculated increase in C_{ant} (ΔC_{ant}) from 1994 343 344 to 2011, obtained from an eMLR analysis, are shown in figures 4a and 4b, respectively. Both 345 distributions show good consistency with previous studies (Ríos et al., 2010; Wanninkhof et 346 al., 2010; Ríos et al., 2012) and are not dissimilar from each other, with areas of high Cant 347 also demonstrating the highest ΔC_{ant} from 1994-2010/11. The total C_{ant} (Fig 4a) values show 348 an increase in the surface waters compared to that of Rios et al. (2010), calculated from the 349 WOCE '94 A17 dataset, which is consistent with the calculated ΔC_{ant} presented here (Fig. 350 4b). The general pattern is that from 1994 to 2011 the most evident increase in C_{ant} occurred 351 in the upper 1000 dbar, particularly in the southern half of the section, with the ΔC_{ant} 352 increasing towards the surface. The atmosphere is the main source of Cant to the ocean, thus it 353 follows that the waters most recently in contact with the atmosphere will show the greatest 354 ΔC_{ant} . Within the surface waters (<100 dbar) of the section the ΔC_{ant} gradually decreases northwards in a linear relationship with latitude ($R^2 = -0.74$) to a concentration of 0 µmol kg⁻¹ 355 356 just north of the equator (\sim 5°N). Despite containing large quantities of C_{ant} (Fig. 4a), low ΔC_{ant} values (<5 µmol kg⁻¹) have been previously noted in the tropical Atlantic region, to a 357 358 depth of 200 dbar, similar to that observed here (Schneider et al., 2012). The same authors 359 have suggested that greater precipitation in the inter-tropical convergence zone can cause errors in the surface C_{ant} determinations in the tropical Atlantic, due to the related increase in 360 361 revelle factor. In the section presented here the Amazon outflow can also be seen in salinity 362 values, thus a variation in freshwater input may also contribute to errors in the method. 363

The largest increase (up to 37 μ mol kg⁻¹) in surface waters was found in the SAZ, just south 364 365 of 45°S, in agreement with the findings of Wanninkhof et al. (2010). The steepest vertical 366 gradient of ΔC_{ant} is found in the same region, at ~47°S just north of the SAF, where over a depth range of 0-600 dbar the ΔC_{ant} decreases from 37 to 0 μ mol kg⁻¹. Further north, the 367 deepest penetration of positive ΔC_{ant} values in the southern half of the section is found at 368 369 1200 dbar in the STZ, between 25°S and 40°S. The ΔC_{ant} zero-contour shoals southward of 370 35°S to ~600 dbar at 50°S, coinciding with the lower limits of AAIW, as has been noted in 371 other ocean basins (Sabine et al., 2004). In the northern half of the section, the deepest limit of ΔC_{ant} penetration in AAIW reaches a depth of ~700 dbar at 15°S and north of the equator 372

- 373 the AAIW signal becomes distorted as it mixes with NADW. The NADW shows near-zero
- 374 concentrations of ΔC_{ant} throughout its extent, with the exception of the *u*NADW in the
- equatorial region, which show ΔC_{ant} values up to 5 μ mol kg⁻¹. In *I*NADW and the other deep
- and bottom waters (AABW, lCDW), ΔC_{ant} shows no change or a tendency to negative values.
- 377
- 378 To estimate the rate of increase of C_{ant} in each water mass we identified their respective cores 379 (Fig. 3b) using the water mass descriptions given in Mémery et al. (2000) and Ríos et al. (2012) and averaged their values of ΔC_{ant} . Assuming a constant yearly increase, we then 380 381 divided this total increase by 17 to obtain the rate of yearly increase of Cant over the period 1994 to 2011. The calculated values are shown in Table 2 with those of Ríos et al. (2012) for 382 383 comparison. The highest rates of increase were found in SACW and SAMW with Cant increase rates of $0.99\pm0.14 \ \mu\text{mol kg}^{-1} \ y^{-1}$ and $0.53\pm0.11 \ \mu\text{mol kg}^{-1} \ y^{-1}$, respectively. The latter 384 385 value shows good consistency with that calculated by Ríos et al. (2012; $0.53\pm0.02 \mu$ mol kg⁻¹ y^{-1}). However, there is a notable difference of 0.09 µmol kg⁻¹ y⁻¹ between the increase for 386 SACW calculated here and that of $0.90\pm0.04 \mu mol \text{ kg}^{-1} \text{ y}^{-1}$ (Ríos et al., 2012). As this is a 387 388 surface water mass, and our study utilized data collected 6 years after that used for 389 comparison in Ríos et al. (2012), we corrected the ΔC_{ant} accordingly. Assuming equilibration between the atmosphere and ocean we corrected our ΔC_{ant} value for the additional DIC 390 391 increase caused solely by atmospheric increases over the last 6 years. The resulting calculated $C_{ant}^{1994-2005}$ increase rate was 0.92±0.14 µmol kg⁻¹ y⁻¹, making our result consistent with the 392 previous estimate. As such, we attribute the difference in calculated ΔC_{ant} increase rates in 393 SACW to the increase in DIC driven by higher atmospheric pCO_2 concentrations in 2010/11. 394 395

Despite the similarities in formation history between SAMW and AAIW, the latter shows a 396 much lower C_{ant} increase rate of 0.37±0.06 umol kg⁻¹ yr⁻¹. The discrepancy between the C_{ant} 397 increase rates in these two water masses is in line with the differences in air-sea CO₂ flux in 398 399 the region (McNeil et al., 2007). In the SAZ a combination of biological production and 400 temperature variability leads to a large seasonal signal of pCO₂. The SAMW is formed in the 401 SAZ, where there is high biological production in spring and summer and wintertime cooling 402 of surface waters. The wintertime cooling effect on the solubility of CO₂ is sufficient to 403 counteract the increase in DIC from mixing, resulting in a strong year-round CO₂ sink. South

404 of the SAF, where AAIW is formed, similar processes operate, however the biological

- 405 production is lower, and convective wintertime mixing brings up high-DIC waters, thus
- 406 reducing the CO_2 sink (McNeil et al., 2007). It has also been shown that in the Indian Ocean
- 407 the formation rate of AAIW is less than that of SAMW, which facilitates more efficient
- 408 sequestration of C_{ant} by the latter (Hartin et al., 2011).
- 409
- 410 Modest increase rates of $0.33\pm0.07 \ \mu mol \ kg^{-1} \ y^{-1}$ and $0.20\pm0.03 \ \mu mol \ kg^{-1} \ y^{-1}$ were calculated
- 411 for *u*CDW and *u*NADW, respectively. Both these water masses have been fairly recently
- 412 ventilated, allowing modest increases in ΔC_{ant} . The increase rate for *u*NADW is in line with
- 413 values found by Perez et al. (2010). Due to the very low ΔC_{ant} values found in *l*NADW and
- 414 *l*CDW, their respective increase rates are not significant and are not discussed further. In
- 415 contrast to our calculated ΔC_{ant} , a number of studies have found increasing concentrations of
- 416 C_{ant} in AABW (Murata et al., 2008; Vázquez-Rodríguez et al., 2009a; Brown et al., 2010).
- 417 However, it has been noted previously that it is absent in eMLR analyses (Wanninkhof et al.,
- 418 2010). The distributions of C_{ant} in AABW presented in Vázquez-Rodríguez et al. (2009a) also
- 419 indicate that C_{ant} concentrations have not yet spread further north than 50°S, potentially
- 420 explaining its absence in our analysis.
- 421

422 5.2 Associated changes of pH

- 423 Assuming no changes of A_T between the WOCE '94 A17 and GEOTRACES-NL
- 424 (2010/2011) occupations, we use the ΔC_{ant} calculated by eMLR and the measured A_T during
- 425 GEOTRACES-NL (2010/2011) to calculate the anthropogenic driven change in pH from
- 426 1994 to 2011 ($\Delta p H^{1994-2011}$). From the application of the φC_T^{0} method of anthropogenic
- 427 carbon determination (Sect. 2.3.2) to the WOCE '94 A17 dataset, we obtain the total C_{ant}
- 428 signal from pre-industrial times to 1994 (Fig. 4a). The C_{ant} value allows the calculation of the
- 429 decline in pH, which has been caused by increasing C_{ant}, during this time period (from pre-
- 430 industrial times to 1994: $\Delta p H^{1994}$). The average surface (<250 dbar) $\Delta p H^{1994}$ across the
- 431 section was -0.08, which is just under the predicted, general surface ocean decrease of 0.1
- 432 (Orr et al., 2005). The ocean interior experienced relatively small $\Delta p H^{1994}$, however, the
- 433 change was accompanied by a significant shoaling of the aragonite saturation horizon, most
- 434 notably in the southern half of the section (Fig. 4c). From pre-industrial times to 1994, south
- 435 of the SAF, at ~49°S, the aragonite saturation horizon rose by ~250 m whereas further north,

436 at 25°S, it has risen just 200 m. The change was almost imperceptible north of the Equator.

437 From 1994 to 2011, $\Delta p H^{1994-2011}$, there is a further decline of 0.03 units, making the total

438 surface $\Delta p H^{2011}$ -0.11 units since pre-industrial times. Thus, of the total decrease since pre-

439 industrial times to the present day, 27% occurred within the past 17 years. However, we can

440 detect no notable change to the aragonite saturation horizon over the past 17 years (Fig. 4c).

Historically, the uptake of C_{ant} by the surface ocean was relatively gradual, which allowed it

to be well distributed throughout the water column. In contrast, the effects of the more recent,

steeply increasing, anthropogenic acidification have not yet significantly penetrated into thedeeper ocean.

445

The distribution of $\Delta p H^{1994-2011}$ across the section broadly follows the C_{ant} increases (compare 446 Figs 4b 4c), as expected under the assumption of constant A_T. If we further assume a constant 447 decrease over the 17 years, the yearly acidification rates were calculated from $\Delta p H^{1994-2011}$ 448 and identified for each water mass core, as done for the yearly C_{ant} increases (Table 2). The 449 450 highest rates of acidification were found in the surface waters, where we also observe the greatest rates of C_{ant} increase, with SACW showing a rate of pH decrease of 0.0016 yr⁻¹. The 451 452 latter value is in line with that calculated for the same water mass on the eastern side of the North Atlantic Ocean at the ESTOC site (0.0017 yr⁻¹) for the period 1995 to 2004 (Santana-453 454 Casiano et al., 2007; González-Dávila et al., 2011). The SAMW demonstrates the next greatest rate of decline of 0.0014 y⁻¹, followed by AAIW and *u*CDW both showing 455 acidification rates of 0.001 yr^{-1} , which are comparable with values from other recently 456 ventilated water masses in the North Atlantic: acidification rates of 0.0019 yr⁻¹ and 0.0012 yr⁻¹ 457 ¹ have been reported for SubArctic Intermediate Water and SubPolar Mode Water, 458 459 respectively (Vázquez-Rodríguez et al., 2012). The lowest non-zero acidification rate of 0.0005 yr^{-1} is found in *u*NADW. 460

461

462 **5.3 Buffering Capacity**

The continuing uptake of atmospheric CO₂ gradually depletes the naturally available

464 carbonate ion in the surface ocean thereby decreasing the capacity to 'buffer' further CO_2

465 uptake and leading to the gradual acidification of the seawater. The extent to which the pH is

- 466 affected by the increase of DIC is dependent upon several properties, including temperature,
- 467 pressure, and A_T, which together determine the *buffering capacity* of the water. As DIC

468 increases, assuming no other changes take place, the buffering capacity of the water is reduced as $[CO_3^{2-}]$ decreases and $[CO_2]$ increases. The A_T is not altered by the flux of 469 470 atmospheric CO₂ into the ocean. However, A_T is affected by biological processes, notably the 471 dissolution and formation of calcium carbonate, with dissolution dominating in deep waters 472 and formation playing a more important role in the surface. Table 2 quantifies the extent to 473 which the calculated ΔC_{ant} have impacted pH in the water masses of the southwest Atlantic Ocean. Examination of this table clearly shows that the rate of acidification per μ mol kg⁻¹ of 474 DIC is not equal between water masses. The SAMW, a relatively fresh, low alkalinity water 475 mass, has an acidification rate of -0.0014 yr⁻¹, which is 88% of that of SACW, a warmer, 476 477 more saline water mass. However, the Cant increase rate of SAMW is only 54% that of 478 SACW. The AAIW shows the same rate of acidification as *u*CDW, however, the increase of C_{ant} in *u*CDW is 10% lower than that of AAIW. These differences can be attributed to the 479 480 varying buffering capacities of the water masses.

481

482 The distributions of the revelle factor and the sensitivities of $[H^+](\beta DIC)$, $[CO_2](\gamma DIC)$ and 483 Ω_{CaCO3} (ω DIC) to changes in DIC for the southwest Atlantic are shown in Fig. 5 and given 484 per water mass in Table 3. The highest buffer factors, which indicate the greatest sensitivities 485 to increasing DIC (denoted by low values in figures 5b, 5c, and high values in 5d) were generally found in the deep waters. That is to say that for a given increase in DIC these 486 waters will show large resultant changes in [H⁺], [CO₂] and [CO₃²⁻], or aragonite and calcite 487 saturation (Ω_{Ar} , Ω_{Ca}). Both *u*CDW and *l*CDW show very similar behavior – as expected from 488 489 their similar history – however, interestingly, there is a notable difference between the 490 buffering capacities of the two limbs of NADW. The difference is most noticeable in ω DIC, 491 likely caused by the slightly higher A_T /DIC ratio in *I*NADW. A lower β DIC in *u*NADW 492 denotes a greater sensitivity to acidification in response to increasing DIC concentrations. 493 More rapid acidification in uNADW, compared to INADW, has been observed by Vázquez-494 Rodríguez et al. (2012) and attributed to mixing with Labrador Sea Water (LSW), which 495 exhibits a strong decreasing pH trend with time. The lower pH of LSW and its contribution to 496 *u*NADW could account for the reduced buffering capacity calculated in this water mass in the 497 southwest Atlantic Ocean.

499 The lowest Revelle Factor, and highest βDIC values are found in SACW, closely followed by 500 SAMW, which despite containing large concentrations of C_{ant}, both have relatively low 501 concentrations of DIC compared to the other water masses. The SACW and SAMW also 502 have higher concentrations of A_T giving them greater buffering capacity. The three water 503 masses with the greatest response in pH relative to ΔC_{ant} were AAIW, uCDW and lCDW, with β DIC values of 0.148 mmol kg⁻¹, 0.141 mmol kg⁻¹, and 0.143 mmol kg⁻¹, respectively. 504 These water masses show the highest DIC/A_T ratios along the section as they all originate in 505 506 the Southern Ocean (SO) where upwelling brings deep waters rich in [CO₂(aq)] and low in 507 $[CO_3^{2^-}]$ to the surface. In addition, these waters have slightly lower salinities and thus lower borate concentrations, which further diminish their buffering capacity, also reflected in the 508 509 high revelle factors (Fig. 5a). For the same DIC value the buffering capacity of AAIW is 510 substantially lower than that of *u*CDW stemming from the low A_T of AAIW, which is also 511 reflected in the high ω DIC values. With the current calculated rate of increase of C_{ant}, 512 aragonite will become under-saturated in AAIW around the year 2100, when DIC concentrations reach 2208 µmol kg⁻¹. This could happen even sooner, as wintertime, storm-513 514 driven upwelling entrainment of deep waters into the surface in the SO is predicted to cause 515 seasonal aragonite under-saturation in the region as soon as 2030, when atmospheric CO_2

516 levels reach ~450 ppm (McNeil and Matear, 2008).

517

518 5.4 Continued C_{ant} increase

519 The buffering capacity of each water mass will be reduced by increasing the DIC

520 concentrations. To investigate how the buffering capacities of the different water masses in

521 this section have changed over time, and will continue to do so, the DIC buffer factors of

522 each water mass were calculated and plotted against DIC concentration (Fig. 6). Due to the

523 large relative error of the calculated ΔC_{ant} increases in the deeper waters, these were not

524 included. The high rate of uptake of C_{ant} by SACW means that this water mass has seen the

525 largest decrease in buffering capacity since pre-industrial times. The β DIC value has

526 decreased from 0.281 to 0.247 mmol kg⁻¹ and Ω_{Ar} has decreased from 4.1 to 3.3. In contrast,

527 uCDW has shown relatively little change due to the low values of C_{ant}. However,

528 extrapolating our calculated C_{ant} rates of increase we predict a 33 µmol kg⁻¹ increase in this

529 water mass over the next century, which will result in a significant reduction in buffering and

a pH decrease of -0.102. The buffering capacities of SAMW and AAIW follow a similar

- 531 pattern to each other, however, SAMW contains a greater proportion of subtropical water
- than AAIW, thus it maintains a slightly higher buffering capacity than AAIW. Both AAIW
- and *u*CDW will see a similar increase in C_{ant} over the next century (37 and 33 μ mol kg⁻¹,
- respectively), however, the decline in Ω_{Ar} will be 1.6 times greater in AAIW, due to higher
- ω DIC values. The SAMW will see approximately 54% of the increase in C_{ant} that SACW
- 536 will experience, however will undergo 84% of the associated pH decline. These extrapolated
- 537 predictions highlight the vulnerability of SAMW and AAIW to increasing C_{ant}, as also noted
- 538 by Gonzalez-Davila et al. (2011).
- 539

540 The observed pattern of ΔC_{ant} in the southwest Atlantic clearly identifies the SAZ as the most 541 effective entry point of C_{ant} into the ocean. In addition, the buffering factors of Egleston et al. 542 (2010) explicitly show that by the end of this century the two dominant water masses in this 543 area (SAMW and AAIW) will be the most sensitive to further Cant increases. Whilst it is clear 544 that this will accelerate the rate of acidification in these water masses, it is unclear how it will 545 affect the CO₂ uptake in the SAZ. Assuming no changes to primary production, the increased 546 sensitivity of SAMW to DIC changes will lead to much greater seasonal variability in the 547 carbonate system of this water mass between the productive and non-productive period. The 548 biological uptake of DIC in the SAZ in austral spring and summer would lead to a more 549 dramatic decrease in surface water pCO₂, allowing a greater air-sea pCO₂ flux. Conversely, 550 the acidification and decline in Ω_{Ar} may be detrimental to calcifying organisms in the area, as 551 observed in the Southern Ocean (Bednarsek et al., 2012), thus limiting export via the 552 biological pump.

553

554 The water masses SAMW and AAIW both risk further reduction in their buffering capacities 555 by long-term variability to their physical properties. On decadal time scales a freshening of 556 AAIW has been observed in the Pacific and Indian sectors of the Southern Ocean (Wong et 557 al., 1999). Decadal variability has also been noted in temperature, salinity and 558 biogeochemical parameters of SAMW (Bindoff et al., 2007; Alvarez et al., 2011), which 559 could further diminish or enhance the buffering capacity of this water mass and thus the Cant 560 driven acidification. Variations on decadal time scales have been related to the Southern 561 Annular Mode, the dominant climate forcing over the region (Lovenduski et al., 2007;

562 Álvarez et al., 2011). Similarly in the North Atlantic, the North Atlantic Oscillation exerts a

563 degree of control over the carbonate system variables and C_{ant} uptake (Santana-Casiano et al.,

564 2007; Pérez et al., 2010). Such external controls will cause irregular C_{ant} uptake over time, as

- 565 has been observed by Brown et al. (2010), making it difficult to accurately predict future C_{ant}
- 566 uptake and associated changes in the buffering capacity.
- 567

568 6 Conclusion

- 569 The continuing uptake of C_{ant} in the southwest Atlantic has been assessed through application
- 570 of eMLR to two datasets collected in 1994 and 2011. The distribution of ΔC_{ant} is comparable
- 571 with previous studies of C_{ant} accumulation in the region (Ríos et al., 2010). The largest
- 572 increases are found in the SAZ, just north of the SAF; a previously identified substantial CO₂
- 573 sink (Metzl et al., 1999). The SACW (0.99 \pm 0.14 µmol kg⁻¹ y⁻¹), SAMW (0.53 \pm 0.11 µmol kg⁻¹
- 574 1 y⁻¹) and AAIW (0.36±0.06 µmol kg⁻¹ y⁻¹) are responsible for the greatest C_{ant} uptake,
- 575 consistent with earlier studies showing them to be an effective pathway of C_{ant} into the ocean
- 576 interior (Álvarez et al., 2009). The lower extent of AAIW demarks the greatest depth of
- 577 penetration of C_{ant} into the ocean in the past 17 years indicating that future uptake will,
- 578 similarly, be largely concentrated within the surface 1000m.
- 579
- 580 The increase in C_{ant} in the southwest Atlantic has led to acidification of water masses. The 581 calculated C_{ant}-driven acidification is greatest in SACW, where a current rate of pH decline of 0.0016 yr⁻¹ is found. However, the acidification response per µmol kg⁻¹ increase in DIC is 582 greatest in the intermediate and mode waters. We identify SAMW as the water mass with the 583 584 greatest risk of rapid acidification in the future, due to a combination of its high C_{ant} uptake 585 and its limited buffering capacity. AAIW, on the other hand, is more at risk of aragonite 586 under-saturation due its low A_T values and resultant high ωDIC values. Continued increase of C_{ant} at the current rate calculated will lead to aragonite under-saturation in the core of AAIW 587 588 around the year 2100.
- 589

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872 Tables

873 **Table 1a.**

| Min | Max | Mea | a | Si(O | NO | Sal | The | AO | Pressu | rms | R ² | n |
|-------|-------|------|---|------|----|-----|-----|----|--------|-----|----------------|---|
| densi | densi | n | | H)4 | 3 | | ta | U | re | e | | |
| ty | ty | Lay | | | | | | | | | | |
| | | er | | | | | | | | | | |
| | | Dept | | | | | | | | | | |
| | | h | | | | | | | | | | |
| | | (m) | | | | | | | | | | |
| | | | | | | | | | | | | |

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Sigma-0
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| 20.0 | 23.5 | 31 | 131 | 1.61 | 33.9 | 56.25 | - | - | 0.208 | 7.6 | 0.9 | 90 |
|------|------|-----|-----|--------|------|-------|------|------|--------|-----|-----|----|
| | | | | | 1 | | 4.78 | 0.08 | | | 8 | |
| 23.5 | 24.5 | 50 | 656 | -1.73 | 14.1 | 42.36 | - | 0.35 | -0.011 | 6.3 | 0.9 | 73 |
| | | | | | 3 | | 5.56 | | | | 5 | |
| | | | | | | | | | | | | |
| 24.5 | 25.0 | 53 | 152 | -23.36 | 17.8 | 60.70 | - | 0.22 | -0.262 | 5.0 | 0.9 | 23 |
| | | | | | 6 | | 11.3 | | | | 9 | |
| | | | | | | | 3 | | | | | |
| | | | | | | | | | | | | |
| 25.0 | 25.4 | 57 | 711 | -7.00 | 2.69 | 41.06 | - | 0.83 | -0.094 | 5.5 | 0.9 | 45 |
| | | | | | | | 5.12 | | | | 9 | |
| | | | | | | | | | | | | |
| 25.4 | 26.2 | 107 | 157 | -4.99 | 1.85 | 14.10 | - | 0.74 | 0.008 | 3.8 | 0.9 | 84 |

| | | | 7 | | | | 0.08 | | | | 9 | |
|------|------|------|----------|-------|------|-------|-----------|------|--------|-----|----------|----|
| 26.2 | 26.4 | 160 | 120 6 | -0.35 | 1.36 | 26.14 | - 3.38 | 0.57 | -0.017 | 2.1 | 1.0 0 | 45 |
| 26.4 | 26.6 | 196 | 825 | -0.35 | 3.68 | 36.18 | - | 0.23 | 0.003 | 2.4 | 1.0 | 72 |
| 26.6 | 26.8 | 259 | 124 | -0.42 | 2.77 | 24.17 | - | 0.33 | -0.004 | 1.7 | 0 1.0 | 67 |
| 26.8 | 27.0 | 310 | 9 111 | -0.33 | 2.22 | 28.72 | 1.56 - | 0.37 | -0.012 | 1.6 | 0 1.0 | 10 |
| | | | 6 | | | | 3.30 | | | | 0 | 9 |
| 27.0 | 27.2 | 431 | 136 | 0.97 | 4.33 | 18.81 | 3.61 | 0.06 | -0.002 | 1.1 | 1.0 | 11 |
| | | | 6 | | | | | | | | 0 | 2 |
| 27.2 | 27.4 | 672 | 601 | 0.45 | 3.58 | 42.68 | - 3.07 | 0.16 | -0.004 | 2.1 | 0.9 9 | 96 |
| 27.4 | 27.5 | 991 | 257 | 0.77 | - | - | - | 0.72 | 0.006 | 1.4 | 0.9 | 42 |
| | | | 5 | | 0.38 | 13.66 | 3.01 | | | | 8 | |
| | | | | | Sig | gma-2 | | | | | | |
| 27.5 | 36.7 | 1108 | 205 | 0.65 | - | 3.57 | - | 0.88 | -0.005 | 1.5 | 0.9 | 40 |
| | | | 6 | | 2.40 | | 8.06 | | | | 9 | |
| 36.7 | 36.8 | 1279 | 147 | 0.88 | - | 20.18 | - | 1.05 | 0.003 | 1.0 | 1.0 | 44 |

| | | | 1 | | 3.58 | | 7.86 | | | | 0 | |
|------|------|------|-----|------|------|-------|------|------|-------|-----|-----|----|
| 36.8 | 36.9 | 1531 | 468 | 1.43 | - | - | 17.1 | 0.45 | 0.003 | 1.2 | 1.0 | 58 |
| | | | 3 | | 2.57 | 74.16 | 4 | | | | 0 | |
| 36.9 | 36.9 | 1614 | 484 | 1.12 | - | - | 10.8 | 0.45 | 0.001 | 1.2 | 1.0 | 31 |
| | | | 0 | | 2.24 | 77.82 | 7 | | | | 0 | |
| 36.9 | 37.0 | 1946 | 768 | 1.50 | - | - | 19.1 | 0.45 | 0.003 | 2.3 | 1.0 | 10 |
| | | | 6 | | 4.85 | 158.8 | 9 | | | | 0 | 9 |
| | | | | | | 9 | | | | | | |
| 37.0 | 37.1 | 2586 | 693 | 0.90 | - | - | 8.11 | 0.63 | 0.002 | 0.7 | 1.0 | 71 |
| | | | 7 | | 3.65 | 137.0 | | | | | 0 | |
| | | | | | | 1 | | | | | | |

| | Sigma-4 | | | | | | | | | | | |
|------|---------|------|-----|------|------|-------|------|------|--------|-----|-----|----|
| 37.1 | 45.9 | 3050 | 180 | 0.35 | 0.79 | 10.42 | - | 0.42 | -0.005 | 0.7 | 0.9 | 17 |
| | | | 8 | | | | 15.6 | | | | 9 | 4 |
| | | | | | | | 8 | | | | | |
| 45.9 | 46.0 | 3730 | 308 | 0.29 | - | - | - | 0.75 | 0.001 | 1.2 | 1.0 | 12 |
| | | | 7 | | 0.49 | 27.18 | 8.62 | | | | 0 | 2 |
| 46.0 | 46.0 | 4195 | - | 0.43 | 3.45 | 460.1 | - | 1.04 | 0.005 | 1.4 | 1.0 | 43 |
| | | | 140 | | | 9 | 21.0 | | | | 0 | |
| | | | 16 | | | | 3 | | | | | |

| | 46.0 | 46.1 | 4582 | - | 0.40 | - | 258.0 | 23.2 | 1.15 | 0.005 | 1.0 | 0.9 | 68 |
|-----|------|------|------|-----|-------|------|-------|------|------|-------|-----|-----|----|
| | | | | 687 | | 0.61 | 2 | 0 | | | | 9 | |
| | | | | 9 | | | | | | | | | |
| | 46.1 | 60.0 | 5108 | 421 | -0.63 | - | - | 28.2 | 1.85 | 0.011 | 1.1 | 0.8 | 62 |
| | | | | 32 | | 0.99 | 1154. | 5 | | | | 9 | |
| | | | | | | | 59 | | | | | | |
| 874 | | | | | | | | | | | | | |
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| 886 | | | | | | | | | | | | | |

| Min | Max | Mea | a | Si(OH | NO | Sal | Thet | AO | Pressu | rms | R ² | n |
|-------|-------|------|-----|-------|------|-------|------|------|--------|-----|----------------|----|
| densi | densi | n | |)4 | 3 | | a | U | re | e | | |
| ty | ty | Laye | | | | | | | | | | |
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| | | h | | | | | | | | | | |
| | | (m) | | | | | | | | | | |
| | | | | | Sig | gma-θ | | | | | | |
| 20.0 | 23.5 | 31 | 263 | 7.28 | - | 43.7 | 5.95 | - | -0.047 | 8.6 | 0.9 | 42 |
| | | | | | 96.3 | 7 | | 0.20 | | | 2 | |
| | | | | | 5 | | | | | | | |
| 23.5 | 24.5 | 50 | 466 | -8.70 | 29.3 | 44.6 | - | 0.50 | 0.024 | 8.4 | 0.9 | 15 |
| | | | | | 2 | 5 | 1.93 | | | | 3 | 0 |
| 24.5 | 25.0 | 53 | 105 | -0.11 | 5.00 | 28.9 | - | 0.45 | 0.107 | 2.9 | 0.9 | 56 |
| | | | 2 | | | 6 | 2.49 | | | | 9 | |
| 25.0 | 25.4 | 57 | 125 | -3.68 | 2.04 | 22.2 | - | 0.62 | 0.212 | 6.4 | 0.9 | 57 |
| | | | 9 | | | 1 | 0.65 | | | | 5 | |
| 25.4 | 26.2 | 107 | 974 | 1.55 | 2.21 | 31.4 | - | 0.53 | 0.061 | 6.8 | 0.9 | 13 |
| | | | | | | 3 | 2.76 | | | | 8 | 7 |
| 26.2 | 26.4 | 160 | 109 | 0.62 | 2.93 | 27.8 | - | 0.43 | 0.008 | 3.8 | 0.9 | 75 |
| | | | 7 | | | 2 | 1.96 | | | | 9 | |
| 26.4 | 26.6 | 196 | 964 | 0.58 | 3.55 | 31.3 | - | 0.29 | 0.015 | 3.4 | 0.9 | 89 |

| | | | | | | 6 | 1.47 | | | | 9 | |
|------|------|------|-----|------|------|-------|--------------|------|--------|-----|-----|----|
| 26.6 | 26.8 | 259 | 132 | 0.88 | 4.27 | 19.8 | 1.84 | 0.17 | 0.005 | 2.5 | 1.0 | 10 |
| | | | 6 | | | 7 | | | | | 0 | 4 |
| 26.8 | 27.0 | 310 | 140 | 1.00 | 3.92 | 17.8 | 1.83 | 0.18 | -0.001 | 2.5 | 1.0 | 15 |
| | | | 5 | | | 2 | | | | | 0 | 0 |
| 27.0 | 27.2 | 431 | 144 | 0.84 | 3.36 | 17.2 | 0.64 | 0.22 | -0.004 | 3.5 | 0.9 | 19 |
| | | | 8 | | | 1 | | | | | 9 | 7 |
| 27.2 | 27.4 | 672 | 133 | 0.66 | 2.29 | 21.8 | - | 0.32 | -0.004 | 3.4 | 0.9 | 27 |
| | | | 1 | | | 0 | 2.33 | | | | 9 | 2 |
| 27.4 | 27.5 | 991 | 110 | 0.76 | 1.39 | 28.9 | - | 0.37 | -0.004 | 4.2 | 0.7 | 74 |
| | | | 9 | | | 6 | 3.64 | | | | 5 | |
| | | | | | Sig | gma-2 | | | | | | |
| 27.5 | 36.7 | 1108 | 191 | 0.41 | 1.44 | 5.68 | - | 0.37 | 0.005 | 2.0 | 0.9 | 90 |
| | | | 5 | | | | 3.05 | | | | 8 | |
| 36.7 | 36.8 | 1279 | 127 | 0.53 | 0.47 | 25.0 | - | 0.55 | -0.002 | 1.7 | 1.0 | 32 |
| | | | 2 | | | 6 | 8. 77 | | | | 0 | |
| 36.8 | 36.9 | 1531 | 147 | 0.76 | 1.57 | 18.1 | - | 0.30 | -0.003 | 5.3 | 0.9 | 10 |
| | | | 3 | | | 7 | 0.31 | | | | 8 | 5 |
| 36.9 | 36.9 | 1614 | 327 | 0.82 | 1.18 | - | 4.65 | 0.20 | -0.002 | 2.8 | 0.9 | 94 |
| | | | 8 | | | 33.6 | | | | | 9 | |
| | | | | | | 6 | | | | | | |
| 36.9 | 37.0 | 1946 | 437 | 0.76 | 1.43 | - | 5.14 | 0.11 | 0.001 | 2.2 | 1.0 | 22 |
| | | | 2 | | | 65.0 | | | | | 0 | 6 |

| | 37.0 | 37.1 | 2586 | 389 | 0.36 | 1.15 | - | - | 0.43 | 0.002 | 1.9 | 1.0 | 19 |
|-----|------|------|------|-----|------|------|-------|------|------|-------|-----|-----|----|
| | | | | 9 | | | 51.1 | 1.59 | | | | 0 | 4 |
| | | | | | | | 6 | | | | | | |
| | | | | | | Sig | gma-4 | | | | | | |
| | 37.1 | 45.9 | 3050 | 133 | 0.53 | 2.11 | 21.8 | - | 0.29 | 0.002 | 1.7 | 0.9 | 14 |
| | | | | 5 | | | 3 | 2.35 | | | | 8 | 5 |
| | 45.9 | 46.0 | 3730 | 303 | 0.64 | 1.53 | - | 4.95 | 0.21 | 0.003 | 1.8 | 1.0 | 26 |
| | | | | 6 | | | 27.1 | | | | | 0 | 8 |
| | | | | | | | 1 | | | | | | |
| | 46.0 | 46.0 | 4195 | 800 | 0.09 | 1.73 | - | - | 0.23 | 0.003 | 2.6 | 0.9 | 75 |
| | | | | 8 | | | 168. | 0.95 | | | | 9 | |
| | | | | | | | 68 | | | | | | |
| | 46.0 | 46.1 | 4582 | 810 | 0.06 | 0.32 | 38.1 | - | 0.77 | 0.005 | 3.0 | 0.6 | 16 |
| | | | | | | | 2 | 13.2 | | | | 0 | 5 |
| | | | | | | | | 9 | | | | | |
| | 46.1 | 60.0 | 5108 | _ | 0.00 | 0.30 | 230. | _ | 0.80 | 0.003 | 1.2 | 0.7 | 10 |
| | | | | 586 | | | 89 | 27.0 | | | | 4 | 8 |
| | | | | 7 | | | 07 | 7 | | | | - | Ū |
| 388 | | | | | | | | - | | | | | |

| Water | Density | Latitude | Pressure | dC _{ant} /dt | dC_{ant}/dt^{a} | dpH/dt |
|---------------|------------------------|-------------------|-----------|------------------------|------------------------|---------------------|
| Mass | Range | | (dbar) | (µmol kg ⁻¹ | (µmol kg ⁻¹ | (yr ⁻¹) |
| | | | | yr ⁻¹) | yr ⁻¹) | |
| <u>CACW</u> | | 2295 | 00.170 | 0.00+0.14 | 0.00+0.04 | 0.0016 |
| SAC W | σ °20 - | 23 8 - | 90-160 | 0.99±0.14 | 0.90±0.04 | -0.0016 |
| | σº26.8 | 18°S | | | | |
| | | 509 0 | 00.170 | 0 52 10 11 | 0.52 + 0.02 | 0.0014 |
| SANIW | σ•26.8 - | 50*5- | 90-160 | 0.55±0.11 | 0.53±0.02 | -0.0014 |
| | σº27.1 | 48°S | | | | |
| A A TXX/ | ~.71 | 50° S | 260 450 | 0.2610.06 | 0.2610.06 | 0.0010 |
| | 0°27.1 - | 30 8 - | 300-430 | 0.30±0.00 | 0.30±0.00 | -0.0010 |
| | σ •27.4 | 48°S | | | | |
| <i>uCDW</i> | ci)7 / | 50° S | 1400 1800 | 0 33±0 07 | 0 16+0 04 | 0.0010 |
| ucdw | 0.27.4 - | 30 5 - | 1400-1000 | 0.55±0.07 | 0.10-0.04 | -0.0010 |
| | σ ³ 41.47 | 49°S | | | | |
| <i>u</i> NADW | a•274 - | 10°N – | 1600-1800 | 0 20+0 03 | 0 16+0 04 | -0 0005 |
| | 0 27.1 | 10 11 | 1000 1000 | 0.20-0.00 | 0.10-0.01 | 0.0005 |
| | σ ³ 41.47 | 15°N | | | | |
| <i>I</i> CDW | σ ³ 41.47 - | 50°S – | 3250-3750 | 0±0.06 | 0.08±0.04 | 0.0000 |
| | | 400.0 | | | | |
| | σ ⁴45.9 | 48°5 | | | | |
| <i>I</i> NADW | σ ³ 41.47 - | 10°N – | 3000-3500 | 0±0.02 | 0.08±0.04 | 0.0000 |
| | | 1 - 0 > 1 | | | | |
| | σ445.9 | 15 ⁻ N | | | | |
| | | | | | | |

895 Table 3.

| Water | Salinity | Theta | γDIC | βDIC | ωDIC | Revelle |
|-------|----------|--------|-----------------------|-----------------------|-----------------------|---------|
| Mass | | (°C) | (mmol kg ⁻ | (mmol kg ⁻ | (mmol kg ⁻ | Factor |
| | | | ¹) | ¹) | ¹) | |
| | | | | | | |
| SACW | 36.854 | 22.693 | 0.211 | 0.256 | -0.327 | 10.02 |
| SAMW | 34.021 | 4.4218 | 0.144 | 0.161 | -0.181 | 14.83 |
| AAIW | 34.222 | 2.8567 | 0.136 | 0.149 | -0.165 | 16.02 |
| uCDW | 34.682 | 1.9528 | 0.132 | 0.143 | -0.156 | 17.14 |
| uNADW | 34.987 | 3.8578 | 0.132 | 0.168 | -0.191 | 14.40 |

896

897

898 **Table Captions**

899
Table 1. Calculated coefficients for the performed multi linear regressions for each density
 900 interval using the (a) GEOTRACES-NL (2010/2011) dataset and (b) WOCE '94 A17 dataset. Differences between the coefficients were calculated following equation (2).

901

902

903 Table 2. The calculated rates of increase of C_{ant} and rates of decrease of pH along the section, listed per water mass. The identification criteria for each water mass are provided. Error 904

represents $2\sigma/N^{0.5}$. ^aValues from Ríos et al. [2012]. 905

| 907 | Table 3. The average water mass values of salinity and potential temperature, with |
|-----|--------------------------------------------------------------------------------------------------------------------------------|
| 908 | accompanying average buffering capacity values (γ DIC, β DIC, ω DIC and revelle factor) |
| 909 | calculated using the GEOTRACES-NL (2010/11) dataset. Water masses are determined |
| 910 | using the same criteria as given in Table 2. |
| 911 | |
| 912 | Figure Captions |
| 913 | Figure 1. Stations where DIC and A_T samples were taken from both cruises (black |
| 914 | represents the WOCE '94 A17 stations, red represents the GEOTRACES-NL (2010/2011) |
| 915 | expeditions). |
| 916 | |
| 917 | Figure 2. The residuals of the MLR fits of the (a) WOCE '94 A17 and (b) GEOTRACES-NL |
| 918 | (2010/2011) datasets. |
| 919 | |
| 920 | Figure 3. Section distributions of temperature (°C), salinity, AOU (µmol kg ⁻¹), silicate (µmol |
| 921 | kg ⁻¹), A_T (µmol kg ⁻¹) and DIC (µmol kg ⁻¹) from the GEOTRACES-NL (2010/2011) dataset. |
| 922 | |
| 923 | Figure 4 . Distribution of C_{ant} (µmol kg ⁻¹) calculated using the ϕC_T^0 method with the |
| 924 | GEOTRACES-NL (2010/2011) dataset (top), distribution of $\Delta C_{ant}^{1994-2011}$ (µmol kg ⁻¹), |
| 925 | calculated using the eMLR approach (middle), and the distribution of the $\Delta p H^{1994-2011}$ |
| | |

| 926 | associated with $\Delta C_{ant}^{1994-2011}$ (bottom). The aragonite saturation horizon (ΩAr) is marked on |
|-----|----------------------------------------------------------------------------------------------------------------------|
| 927 | for pre-industrial times (solid line), 1994 (dashed line) and 2011 (dotted line). |

| 929 | Figure 5. 1 | Distribution | of the | Revelle | factor | across | the | section | (top | left) | and | the th | iree |
|-----|-------------|--------------|--------|---------|--------|--------|-----|---------|------|-------|-----|--------|------|
|-----|-------------|--------------|--------|---------|--------|--------|-----|---------|------|-------|-----|--------|------|

- 930 buffering factors relating to DIC; β DIC (top right), γ DIC (bottom left), and ω DIC (bottom
- 931 right). The latter three are all given in mmol kg^{-1} .

- **Figure 6**. The buffer factors β DIC (top), γ DIC (middle), and ω DIC(bottom) of each water
- mass over a range of DIC concentrations. The vertical lines denote the DIC concentration in
- pre-industrial times, 1994, 2011 and the projected concentration in 2110.











