

1 Rapid acidification of mode and intermediate waters in the southwest Atlantic
2 Ocean.

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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
30 that the ΔC_{ant} from 1994 to 2011 has largely remained confined to the upper 1000 dbar. The
31 greatest changes occur in the upper 200 dbar in the SubAntarctic Zone (SAZ), where a
32 maximum increase of $37 \mu\text{mol kg}^{-1}$ is found. South Atlantic Central Water (SACW)
33 experienced the highest rate of increase in C_{ant} , at $0.99 \pm 0.14 \mu\text{mol kg}^{-1} \text{ y}^{-1}$, resulting in a
34 maximum rate of decrease in pH of 0.0016 yr^{-1} . The highest rates of acidification relative to
35 ΔC_{ant} , however, were found in SubAntarctic Mode Water (SAMW) and Antarctic
36 Intermediate Water (AAIW). The low buffering capacity of SAMW and AAIW combined
37 with their relatively high rates of C_{ant} increase of $0.53 \pm 0.11 \mu\text{mol kg}^{-1} \text{ y}^{-1}$ and 0.36 ± 0.06
38 $\mu\text{mol kg}^{-1} \text{ y}^{-1}$, respectively, has lead to rapid acidification in the SAZ, and will continue to do
39 so whilst simultaneously reducing the chemical buffering capacity of this significant CO_2
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 C_{ant} 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
48 in the past decade the South Atlantic has been more effective at sequestering C_{ant}
49 (Wanninkhof et al., 2010) than the North Atlantic. These authors calculated a rate of increase
50 of the North Atlantic inventory of $1.9 \text{ Pg C decade}^{-1}$, whereas the South Atlantic inventory
51 grew at a rate of $3.0 \text{ Pg C decade}^{-1}$. Calculations by Ríos et al. (2012) indicate that the
52 southwestern Atlantic Ocean dominates the South Atlantic sink of C_{ant} , with a storage rate of
53 $0.25 \pm 0.035 \text{ Pg C decade}^{-1}$. Quantifying the exact rate of increase in anthropogenic carbon in
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 ($\sim 3\%$; Ríos et al., 2010). In the past decade a number
57 of methods for calculating the increase in C_{ant} (ΔC_{ant}) between reoccupation of ocean transects
58 have been developed (TrOCA, φC_T^0 , eMLR). Despite the differing approaches and
59 assumptions, there is overall coherence in the determinations of the anthropogenic

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

62

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

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 ($[\text{H}^+]$, $[\text{HCO}_3^-]$,
83 $[\text{CO}_2]$) and decreasing carbonate concentrations ($[\text{CO}_3^{2-}]$), a process referred to as *ocean*
84 *acidification*. Sabine et al. (2004) state that approximately 50% of the total amount of C_{ant} in
85 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.,
87 2005) and is ongoing. Observations have found acidification rates of $0.0016 \pm 0.0001 \text{ yr}^{-1}$ and
88 $0.0012 \pm 0.002 \text{ yr}^{-1}$, in the North Atlantic Ocean, for Subarctic Intermediate Water (SAIW)
89 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 $0.0017 \pm 0.0004 \text{ yr}^{-1}$, 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 ($[\text{CO}_2(\text{aq})]$), in particular Antarctic
101 Intermediate Water (AAIW) and upper Circumpolar Deep Water (uCDW) 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 (CaCO_3), 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 CaCO_3 resulting in a saturation horizon ($\Omega_{\text{Ar}}=1$) approximately 2 km
109 shallower than that of calcite in the South Atlantic Ocean, below which depth the CaCO_3
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 ($p\text{CO}_2$) (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
114 species are already being affected by C_{ant} accumulation. Organisms that use aragonite are
115 thus much more vulnerable to decreases in $[\text{CO}_3^{2-}]$ driven from the surface increase in $[\text{CO}_2]$.

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.

123

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
129 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
133 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 $\mu\text{mol kg}^{-1}$ 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
142 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
148 samples of 600 ml were collected from throughout the water column, from 24 Niskin
149 samplers mounted onto a CTD rosette, following standard operating procedures (Dickson et
150 al., 2007). At least two duplicate 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,
153 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
155 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 $\pm 1.0 \mu\text{mol kg}^{-1}$ and
159 the precision of A_T was $\pm 1.1 \mu\text{mol kg}^{-1}$.

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 (PO_4 , Si(OH)_4 , NO_3) were
164 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 ± 0.01 , 0.2 , and $0.2 \mu\text{mol l}^{-1}$ for PO_4 , Si(OH)_4 , and
167 NO_3 , 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 , PO_4), the pH
171 and pCO_2 were also calculated in-situ for both datasets using CO_2_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 KSO_4 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 Deepwater consistency between WOCE and GEOTRACES**

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, NO_3 , Si(OH)_4 and
182 apparent oxygen utilization ($\text{AOU} = [\text{O}_2]_{\text{sat}} - [\text{O}_2]_{\text{obs}}$) and is particularly sensitive to large scale
183 ('secular') changes in the distributions of these properties, as well as to analytical biases in
184 their measurement. In order to assess the magnitude and distributions of these changes, we
185 gridded the values of salinity, DIC, NO_3 , Si(OH)_4 and AOI 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
 189 mass in the section) the differences average -0.01 ± 0.015 (salinity), $-4.2 \pm 12.1 \mu\text{mol kg}^{-1}$
 190 (DIC), $-1.92 \pm 0.78 \mu\text{mol kg}^{-1}$ (NO_3), $-5.05 \pm 3.3 \mu\text{mol kg}^{-1}$ ($\text{Si}(\text{OH})_4$) and $-3.13 \pm 3.9 \mu\text{mol kg}^{-1}$
 191 (AOU).

192

193 **3 Methods**

194 **3.1 eMLR and C_{ant} Calculations**

195 There are two general carbon data-based approaches for studying the increasing oceanic C_{ant} .
 196 The first approach uses back-calculation techniques to obtain an estimate of pre-industrial
 197 DIC concentration against which to compare current measurements. Methods from the
 198 second approach aim to determine the part of change in DIC between two specific time
 199 periods that is attributable to anthropogenic invasion. One example of each approach is
 200 employed in this study; eMLR (Friis et al., 2005) and φC_T (Vázquez-Rodríguez et al., 2009a,
 201 2009b). Various comparison and evaluations of these and other methods are available in the
 202 literature (Levine et al., 2008; Yool et al., 2010; van Heuven et al., 2011b; Sabine and
 203 Tanhua, 2010).

204

205 **3.1.1 ΔC_{ant} from eMLR**

206 The multi-linear regression approach to estimating anthropogenic CO_2 invasion was
 207 introduced by Wallace (1995). It involves using a number of biogeochemical properties,
 208 known to be related to DIC, to obtain a model of the observed DIC. As the relationships
 209 between DIC and these properties are expected not to change over time, the same statistical
 210 relationships can be applied to a second dataset of later date. Differences between the thus
 211 ‘predicted’ DIC and the observed DIC are attributed to the invasion of anthropogenic CO_2 . In
 212 the extended version (eMLR) developed by Friis et al. (2005), which is applied here, the DIC
 213 from two datasets is fitted to the same selection of properties from both datasets, and the
 214 difference between parameter coefficients is assumed to be predictive of the difference in C_{ant}
 215 between the two cruises:

$$216 \quad \Delta C_{\text{ant}}^{\text{eMLR}} = \text{DIC}^{\text{MLR2,t2}} - \text{DIC}^{\text{MLR1,t1}} \quad (1)$$

$$217 \quad = (a_2 - a_1) + (b_2 - b_1) \text{SiO}_{2\text{t2}} + (c_2 - c_1) \text{NO}_{3\text{t2}} + (d_2 - d_1) \text{AOU}_{\text{t2}} + (e_2 - e_1)$$

218
$$S_{t2} + (f_2 - f_1) T_{t2} + (g_2 - g_1) P_{t2} \quad (2)$$

219 Following equation 2, we apply the backward calculation technique as the DIC data from the
220 more recent GEOTRACES-NL (2010/2011) cruise demonstrates a greater precision. The
221 properties used to predict DIC in the WOCE '94 dataset results in an R^2 value of 0.97 and a
222 root mean square error (rmse) of $10.7 \mu\text{mol kg}^{-1}$. For the GEOTRACES-NL (2010/2011)
223 dataset a R^2 of 0.98 was obtained and a rmse of $9.9 \mu\text{mol kg}^{-1}$ (Fig. 2).

224

225 The eMLR regressions were applied along isopycnals intervals, as the preferred method of
226 water movement from the surface into the ocean interior is along surfaces of constant density.
227 It thus follows that waters occupying the same density band share a common formation
228 history and can be described by a single equation. Isopycnal bands were chosen based on
229 temperature-salinity plots of the water masses and the amount of data occupying each
230 interval. The coefficients and accompanying statistics from each isopycnal interval are
231 displayed in Table 1(a) and (b) for the 1994 and 2010/11 regressions, respectively. The
232 residuals of each fit are shown in Fig. 2, with the 2011 dataset showing an average of 2.1
233 $\mu\text{mol kg}^{-1}$ in the more stable deeper waters (>2000 dbar). In comparison, the WOCE '94 A17
234 dataset shows a deep water (>2000 dbar) column average residual of $3.17 \mu\text{mol kg}^{-1}$, which
235 we attribute to less precise measurements in the earlier dataset. Pressure was included in the
236 regression to avoid skewing (over depth) of the residuals of the MLR by the relatively large
237 amount of samples located towards the surface, as mentioned by Hauk et al. (2010).

238

239 **3.1.2 C_{ant} from φC_T°**

240 The φC_T° method is a back-calculation approach that uses stoichiometric ratios from
241 biogeochemical processes to account for the addition of DIC in the water column resulting
242 from organic matter remineralization and calcium carbonate dissolution, since the time of
243 water formation (Vázquez-Rodríguez, 2008; Vázquez-Rodríguez et al. 2009a). It is based on
244 the general principle of 'preformed DIC' (or C_T°) of Brewer (1978) and ΔC^* of Gruber et al.
245 (1996). The main advantage of this method is that it considers the non-steady state of A_T and
246 $p\text{CO}_2$ in the subsurface reference layer.

247

248 **3.2 Buffer Factors**

249 The *revelle factor* was originally described by Revelle and Suess (1957) and quantified the

250 attenuated response of increasing DIC impacted by increasing pCO₂, or vice versa. This work
 251 has been built upon by Egleston et al. (2010), who outlined six expressions that define how
 252 [CO₂], [H⁺], and Ω_{Ar} or Ω_{Ca}, are impacted by changes in DIC or A_T. The following three
 253 expressions for the buffer factors relating to DIC were applied to the GEOTRACES-NL
 254 (2010/2011) and WOCE '94 A17 southwest Atlantic sections (Equations (3-4) and (6-7) are
 255 taken from Egleston et al., (2010), however, Equation (5) and (8) are taken from Álvarez et
 256 al., (2014), who identified and corrected a typo in the definitions of Egleston et al., 2010).

$$257 \quad \gamma\text{DIC} = \text{DIC} - \text{Alk}_C^2/S, \quad (3)$$

$$258 \quad \beta\text{DIC} = \text{DIC} \times S - \text{Alk}_C^2/\text{Alk}_C, \quad (4)$$

$$259 \quad \omega\text{DIC} = \text{DIC} - \{\text{Alk}_C \times (2 \times [\text{CO}_2] + [\text{HCO}_3^-])/P\}, \quad (5)$$

$$260 \quad \text{where} \quad \text{DIC} = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}], \quad (6)$$

$$261 \quad \text{Alk}_C = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}], \quad (7)$$

$$262 \quad P = [\text{HCO}_3^-] - \{[\text{H}^+][\text{B}(\text{OH})_4^-]/K_{hb} + [\text{H}^+]\} - [\text{H}^+] + [\text{OH}^-], \quad (8)$$

$$263 \quad S = [\text{HCO}_3^-] + 4[\text{CO}_3^{2-}] + [\text{H}^+] + [\text{OH}^-] + \{[\text{H}^+][\text{B}(\text{OH})_4^-]/K_{hb} + [\text{H}^+]\} \quad (9)$$

264 and Ω refers to the saturation state of sea water with respect to aragonite or calcite. These
 265 equations quantify the resistance to change of [CO₂] (γDIC), [H⁺] (βDIC) and Ω (ωDIC) in a
 266 water mass to changes in DIC. The concentrations used for the calculations were obtained
 267 from CO2SYS (Lewis and Wallace, 1998, adapted for Matlab by van Heuven, 2011a) using
 268 the same input conditions as previously mentioned (Sect. 2.2.3).

269

270 **4 Hydrography of the South Atlantic Ocean**

271 The distributions of potential temperature, salinity, AOU, silicate, A_T, and DIC of the
 272 GEOTRACES-NL (2010/2011) section are shown in Fig. 3. The large water masses have
 273 been described elsewhere (Mémery et al., 2000; Ríos et al., 2010; Wanninkhof et al., 2010),
 274 thus here the treatment is relatively concise. Located deeper than 4500 dbar throughout the
 275 section is Antarctic Bottom Water (AABW), characteristic in its high DIC and AOU. Values
 276 for DIC in this water mass range from 2243 to 2267 μmol kg⁻¹, and AOU values occupy a
 277 narrow band between 111 to 128 μmol kg⁻¹. The DIC maximum (2267 μmol kg⁻¹) and
 278 potential temperature minimum (-0.16°C) are both found in this water mass, which also
 279 shows the deep water (>1000 dbar) A_T maximum (2369 μmol kg⁻¹). These characteristics are
 280 all representative of the old age of the water mass and are caused by the large amount of

281 organic matter remineralization which has taken place within it. The AABW can, most easily,
282 be distinguished from the overlying *lower* Circumpolar Deep Water (*l*CDW), by the high
283 silicate concentrations, which reach values greater than $120 \mu\text{mol kg}^{-1}$ in AABW. Silicate
284 concentrations in the deep waters (>4000 dbar) demonstrate a strong covariance with A_T
285 ($R^2=0.95$), which has been previously noted and stems from the simultaneous dissolution of
286 opaline and calcium carbonate shells from the hard tissue of organisms (Pérez et al., 2002).

287

288 The *l*CDW has a core at approximately 3500 dbar at 50°S , above which it merges into *upper*
289 Circumpolar Deep Water (*u*CDW), with its respective core identified by an oxygen minimum
290 at approximately 1500 m (Mémery et al., 2000). Both branches of CDW display properties
291 similar to that of AABW, as they represent a mixture of AABW and Weddell Sea Deep
292 Water (Wong et al., 1999; Orsi et al., 1999). The *u*CDW and *l*CDW share isopycnals with
293 *upper* North Atlantic Deep Water (*u*NADW) and *lower* North Atlantic Deep Water
294 (*l*NADW), respectively, in the northern half of the section (Fig. 3a). The *u*CDW and
295 *u*NADW, occupy the density band between $\sigma_\theta > 27.4$ and $\sigma_3 < 41.47$, with the front between the
296 two water masses found at approximately 26°N (Mémery et al., 2000). The NADW has been
297 more recently ventilated than CDW and is thus distinguished by lower AOU values of ~ 60
298 $\mu\text{mol kg}^{-1}$ and DIC values lower than $2200 \mu\text{mol kg}^{-1}$. The deeper *l*NADW can be separated
299 from *u*NADW through higher silicate values, which rise to $40 \mu\text{mol kg}^{-1}$, whereas *u*NADW
300 has maximum silicate concentrations of $20 \mu\text{mol kg}^{-1}$ (Fig. 3d). The A_T values are also lower
301 ($\sim 20 \mu\text{mol kg}^{-1}$) in *u*NADW compared to *l*NADW.

302

303 The Antarctic Intermediate Water (AAIW) enters the section at 200 dbar just south of 48°S ,
304 identifiable as a tongue of water with very low salinity and A_T (34.05 and $2275 \mu\text{mol kg}^{-1}$,
305 respectively)(Fig. 3b). The AAIW lies above *u*CDW and below SubAntarctic Mode Water
306 (SAMW) (Peterson and Whitworth, 1989). This water mass is carried northward at
307 intermediate depths between $\sigma_\theta > 27.1$ and $\sigma_\theta < 27.4$ (Ríos et al., 2012) from south of the SAF.
308 In the southwestern Atlantic Ocean AAIW extends further north than in other oceans, due to
309 the western boundary current along the coast of South America (Talley, 1996). The AAIW is
310 a relatively young water mass and has AOU values comparable to NADW ($\sim 50 - 100 \mu\text{mol}$
311 kg^{-1}), however, it can be distinguished from *u*NADW, in its northward reaches, by its

312 elevated silicate concentrations. Situated above the AAIW, the SAMW is often considered a
313 component of the AAIW (McCartney, 1977). This water mass can be easily identified by the
314 tracer $Si^* = [Si(OH)_4] - [NO_3^-]$ which has values from -10 to -15 $\mu\text{mol kg}^{-1}$ in regions of
315 SAMW formation (Sarmiento et al., 2004). The SAMW formation region is located just
316 south of 47°S in the Subantarctic Zone (SAZ), north of the SAF (McCartney, 1977) where
317 deep winter mixing forms this high-oxygen water mass.

318

319 We locate the Subtropical Front (STF) at $\sim 41^\circ\text{S}$, where there is a steep gradient in salinity in
320 the surface 200 dbar. North of the STF, in the surface, and extending northward to a density
321 of $\sigma_\theta < 26.5 \text{ kg m}^{-3}$, is South Atlantic Central Water (SACW; Ríos et al., 2012), heavily
322 depleted in silicate, and with elevated salinity and A_T . Against this background, the two
323 Amazon plumes are very distinct at 5°N and 15°N with salinity and A_T values as low as
324 34.11 and 2265 $\mu\text{mol kg}^{-1}$, and 32.3 and 2157 $\mu\text{mol kg}^{-1}$, respectively. The maximum values
325 of both salinity and A_T correspond with South Atlantic Central Water (SACW) in the
326 subtropics (17°S), reaching absolute maxima of 37.5 and 2456 $\mu\text{mol kg}^{-1}$, respectively, at 50
327 dbar depth. The subtropical part of the SACW that features high salinity and A_T is often
328 referred to as the Salinity Maximum Water (SMW). In this study we make no distinction
329 between SMW and SACW.

330

331 **5 Results and discussion**

332 **5.1 Anthropogenic carbon in the southwest Atlantic Ocean**

333 The distribution of C_{ant} in 2011, calculated using the φC_T° method (Vázquez-Rodríguez,
334 2008; Vázquez-Rodríguez et al. 2009a), and the calculated increase in C_{ant} (ΔC_{ant}) from 1994
335 to 2011, obtained from an eMLR analysis, are shown in figures 4a and 4b, respectively. Both
336 distributions show good consistency with previous studies (Ríos et al., 2010; Wanninkhof et
337 al., 2010; Ríos et al., 2012) and are not dissimilar from each other, with areas of high C_{ant}
338 also demonstrating the highest ΔC_{ant} from 1994-2010/11. The total C_{ant} (Fig 4a) values show
339 an increase in the surface waters compared to that of Rios et al. (2010), calculated from the
340 WOCE '94 A17 dataset, which is consistent with the calculated ΔC_{ant} presented here (Fig
341 4b). The general pattern is that from 1994 to 2011 the most evident increase in C_{ant} occurred
342 in the upper 1000 dbar, particularly in the southern half of the section, with the ΔC_{ant}

343 increasing towards the surface. The atmosphere is the main source of C_{ant} to the ocean, thus it
344 follows that the waters most recently in contact with the atmosphere will show the greatest
345 ΔC_{ant} . Within the surface waters (<100 dbar) of the section the ΔC_{ant} gradually decreases
346 northwards in a linear relationship with latitude ($R^2 = -0.74$) to a concentration of $0 \mu\text{mol kg}^{-1}$
347 just north of the equator ($\sim 5^\circ\text{N}$). Despite containing large quantities of C_{ant} (Fig. 4a), low
348 ΔC_{ant} values ($< 5 \mu\text{mol kg}^{-1}$) have been previously noted in the tropical Atlantic region, to a
349 depth of 200 dbar, similar to that observed here (Schneider et al., 2012). The same authors
350 have suggested that greater precipitation in the inter-tropical convergence zone can cause
351 errors in the surface C_{ant} determinations in the tropical Atlantic, due to the related increase in
352 Revelle factor. In the section presented here the Amazon outflow can also be seen in salinity
353 values, thus a variation in freshwater input may also contribute to errors in the method.

354

355 The largest increase (up to $37 \mu\text{mol kg}^{-1}$) in surface waters was found in the SAZ, just south
356 of 45°S , in agreement with the findings of Wanninkhof et al. (2010). The steepest vertical
357 gradient of ΔC_{ant} is found in the same region, at $\sim 47^\circ\text{S}$ just north of the SAF, where over a
358 depth range of 0-600 dbar the ΔC_{ant} decreases from 37 to $0 \mu\text{mol kg}^{-1}$. Further north, the
359 deepest penetration of positive ΔC_{ant} values in the southern half of the section is found at
360 1200 dbar in the STZ, between 25°S and 40°S . The ΔC_{ant} zero-contour shoals southward of
361 35°S to ~ 600 dbar at 50°S , coinciding with the lower limits of AAIW, as has been noted in
362 other ocean basins (Sabine et al., 2004). In the northern half of the section, the deepest limit
363 of ΔC_{ant} penetration in AAIW reaches a depth of ~ 700 dbar at 15°S and north of the equator
364 the AAIW signal becomes distorted as it mixes with NADW. The NADW shows near-zero
365 concentrations of ΔC_{ant} throughout its extent, with the exception of the *u*NADW in the
366 equatorial region, which show ΔC_{ant} values up to $5 \mu\text{mol kg}^{-1}$. In *l*NADW and the other deep
367 and bottom waters (AABW, *l*CDW), ΔC_{ant} shows no change or a tendency to negative values.

368

369 To estimate the rate of increase of C_{ant} in each water mass we identified their respective cores
370 (Fig. 3b) using the water mass descriptions given in Mémery et al. (2000) and Ríos et al.
371 (2012) and averaged their values of ΔC_{ant} . Assuming a constant yearly increase, we then
372 divided this total increase by 17 to obtain the rate of yearly increase of C_{ant} over the period
373 1994 to 2011. The calculated values are shown in Table 2 with those of Ríos et al. (2012) for

374 comparison. The highest rates of increase were found in SACW and SAMW with C_{ant}
375 increase rates of $0.99 \pm 0.14 \mu\text{mol kg}^{-1} \text{y}^{-1}$ and $0.53 \pm 0.11 \mu\text{mol kg}^{-1} \text{y}^{-1}$, respectively. The latter
376 value shows good consistency with that calculated by Ríos et al. (2012; $0.53 \pm 0.02 \mu\text{mol kg}^{-1}$
377 y^{-1}). However, there is a notable difference of $0.09 \mu\text{mol kg}^{-1} \text{y}^{-1}$ between the increase for
378 SACW calculated here and that of $0.90 \pm 0.04 \mu\text{mol kg}^{-1} \text{y}^{-1}$ (Ríos et al., 2012). As this is a
379 surface water mass, and our study utilized data collected 6 years after that used for
380 comparison in Ríos et al. (2012), we corrected the ΔC_{ant} accordingly. Assuming equilibration
381 between the atmosphere and ocean we corrected our ΔC_{ant} value for the additional DIC
382 increase caused solely by atmospheric increases over the last 6 years. The resulting calculated
383 $C_{\text{ant}}^{1994-2005}$ increase rate was $0.92 \pm 0.14 \mu\text{mol kg}^{-1} \text{y}^{-1}$, making our result consistent with the
384 previous estimate. As such, we attribute the difference in calculated ΔC_{ant} increase rates in
385 SACW to the increase in DIC driven by higher atmospheric pCO_2 concentrations in 2010/11.
386

387 Despite the similarities in formation history between SAMW and AAIW, the latter shows a
388 much lower C_{ant} increase rate of $0.37 \pm 0.06 \mu\text{mol kg}^{-1} \text{yr}^{-1}$. The discrepancy between the C_{ant}
389 increase rates in these two water masses is in line with the differences in air-sea CO_2 flux in
390 the region (McNeil et al., 2007). In the SAZ a combination of biological production and
391 temperature variability leads to a large seasonal signal of pCO_2 . The SAMW is formed in the
392 SAZ, where there is high biological production in spring and summer and wintertime cooling
393 of surface waters. The wintertime cooling effect on the solubility of CO_2 is sufficient to
394 counteract the increase in DIC from mixing, resulting in a strong year-round CO_2 sink. South
395 of the SAF, where AAIW is formed, similar processes operate, however the biological
396 production is lower, and convective wintertime mixing brings up high-DIC waters, thus
397 reducing the CO_2 sink (McNeil et al., 2007). It has also been shown that in the Indian Ocean
398 the formation rate of AAIW is less than that of SAMW, which facilitates more efficient
399 sequestration of C_{ant} by the latter (Hartin et al., 2011).

400

401 Modest increase rates of $0.33 \pm 0.07 \mu\text{mol kg}^{-1} \text{y}^{-1}$ and $0.20 \pm 0.03 \mu\text{mol kg}^{-1} \text{y}^{-1}$ were calculated
402 for $u\text{CDW}$ and $u\text{NADW}$, respectively. Both these water masses have been fairly recently
403 ventilated, allowing modest increases in ΔC_{ant} . The increase rate for $u\text{NADW}$ is in line with
404 values found by Perez et al. (2010). Due to the very low ΔC_{ant} values found in $l\text{NADW}$ and
405 $l\text{CDW}$, their respective increase rates are not significant and are not discussed further. In

406 contrast to our calculated ΔC_{ant} , a number of studies have found increasing concentrations of
407 C_{ant} in AABW (Murata et al., 2008; Vázquez-Rodríguez et al., 2009a; Brown et al., 2010).
408 However, it has been noted previously that it is absent in eMLR analyses (Wanninkhof et al.,
409 2010). The distributions of C_{ant} in AABW presented in Vázquez-Rodríguez et al. (2009a) also
410 indicate that C_{ant} concentrations have not yet spread further north than 50°S, potentially
411 explaining its absence in our analysis.

412

413 **5.2 Associated changes of pH**

414 Assuming no changes of A_T between the WOCE '94 A17 and GEOTRACES-NL
415 (2010/2011) occupations, we use the ΔC_{ant} calculated by eMLR and the measured A_T during
416 GEOTRACES-NL (2010/2011) to calculate the anthropogenic driven change in pH from
417 1994 to 2011 ($\Delta \text{pH}^{1994-2011}$). From the application of the φC_T^0 method of anthropogenic
418 carbon determination (Sect. 2.3.2) to the WOCE '94 A17 dataset, we obtain the total C_{ant}
419 signal from pre-industrial times to 1994 (Fig. 4a). The C_{ant} value allows the calculation of the
420 decline in pH, which has been caused by increasing C_{ant} , during this time period (from pre-
421 industrial times to 1994: ΔpH^{1994}). The average surface (<250 dbar) ΔpH^{1994} across the
422 section was -0.08, which is just under the predicted, general surface ocean decrease of 0.1
423 (Orr et al., 2005). The ocean interior experienced relatively small ΔpH^{1994} , however, the
424 change was accompanied by a significant shoaling of the aragonite saturation horizon, most
425 notably in the southern half of the section (Fig. 4c). From pre-industrial times to 1994, south
426 of the SAF, at ~49°S, the aragonite saturation horizon rose by ~250 m whereas further north,
427 at 25°S, it has risen just 200 m. The change was almost imperceptible north of the Equator.
428 From 1994 to 2011, $\Delta \text{pH}^{1994-2011}$, there is a further decline of 0.03 units, making the total
429 surface ΔpH^{2011} -0.11 units since pre-industrial times. Thus, of the total decrease since pre-
430 industrial times to the present day, 27% occurred within the past 17 years. However, we can
431 detect no notable change to the aragonite saturation horizon over the past 17 years (Fig. 4c).
432 Historically, the uptake of C_{ant} by the surface ocean was relatively gradual, which allowed it
433 to be well distributed throughout the water column. In contrast, the effects of the more recent,
434 steeply increasing, anthropogenic acidification have not yet significantly penetrated into the
435 deeper ocean.

436

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

452

453 **5.3 Buffering Capacity**

454 The continuing uptake of atmospheric CO_2 gradually depletes the naturally available
455 carbonate ion in the surface ocean thereby decreasing the capacity to ‘buffer’ further CO_2
456 uptake and leading to the gradual acidification of the seawater. The extent to which the pH is
457 affected by the increase of DIC is dependent upon several properties, including temperature,
458 pressure, and A_T , which together determine the *buffering capacity* of the water. As DIC
459 increases, assuming no other changes take place, the buffering capacity of the water is
460 reduced as $[\text{CO}_3^{2-}]$ decreases and $[\text{CO}_2]$ increases. The A_T is not altered by the flux of
461 atmospheric CO_2 into the ocean. However, A_T is affected by biological processes, notably the
462 dissolution and formation of calcium carbonate, with dissolution dominating in deep waters
463 and formation playing a more important role in the surface. Table 2 quantifies the extent to
464 which the calculated ΔC_{ant} have impacted pH in the water masses of the southwest Atlantic
465 Ocean. Examination of this table clearly shows that the rate of acidification per $\mu\text{mol kg}^{-1}$ of
466 DIC is not equal between water masses. The SAMW, a relatively fresh, low alkalinity water
467 mass, has an acidification rate of -0.0014 yr^{-1} , which is 88% of that of SACW, a warmer,
468 more saline water mass. However, the C_{ant} increase rate of SAMW is only 54% that of

469 SACW. The AAIW shows the same rate of acidification as *u*CDW, however, the increase of
470 C_{ant} in *u*CDW is 10% lower than that of AAIW. These differences can be attributed to the
471 varying buffering capacities of the water masses.

472

473 The distributions of the Revelle factor and the sensitivities of $[H^+](\beta\text{DIC})$, $[CO_2](\gamma\text{DIC})$ and
474 $\Omega_{\text{CaCO}_3}(\omega\text{DIC})$ to changes in DIC for the southwest Atlantic are shown in Fig. 5 and given
475 per water mass in Table 3. The highest Revelle factors, which indicate the greatest
476 sensitivities to increasing DIC (denoted by low values in figures 5b, 5c, and high values in
477 5d) were generally found in the deep waters. That is to say that for a given increase in DIC
478 these waters will show large resultant changes in $[H^+]$, $[CO_2]$ and $[CO_3^{2-}]$, or aragonite and
479 calcite saturation (Ω_{Ar} , Ω_{Ca}). Both *u*CDW and *l*CDW show very similar behavior – as
480 expected from their similar history – however, interestingly, there is a notable difference
481 between the buffering capacities of the two limbs of NADW. The difference is most
482 noticeable in ωDIC , likely caused by the slightly higher A_T/DIC ratio in *l*NADW. A lower
483 βDIC in *u*NADW denotes a greater sensitivity to acidification in response to increasing DIC
484 concentrations. More rapid acidification in *u*NADW, compared to *l*NADW, has been
485 observed by Vázquez-Rodríguez et al. (2012) and attributed to mixing with Labrador Sea
486 Water (LSW), which exhibits a strong decreasing pH trend with time. The lower pH of LSW
487 and its contribution to *u*NADW could account for the reduced buffering capacity calculated
488 in this water mass in the southwest Atlantic Ocean.

489

490 The lowest Revelle Factor, and highest βDIC values are found in SACW, closely followed by
491 SAMW, which despite containing large concentrations of C_{ant} , both have relatively low
492 concentrations of DIC compared to the other water masses. The SACW and SAMW also
493 have higher concentrations of A_T giving them greater buffering capacity. The three water
494 masses with the greatest response in pH relative to ΔC_{ant} were AAIW, *u*CDW and *l*CDW,
495 with βDIC values of $0.148 \text{ mmol kg}^{-1}$, $0.141 \text{ mmol kg}^{-1}$, and $0.143 \text{ mmol kg}^{-1}$, respectively.
496 These water masses show the highest DIC/A_T ratios along the section as they all originate in
497 the Southern Ocean (SO) where upwelling brings deep waters rich in $[CO_2(\text{aq})]$ and low in
498 $[CO_3^{2-}]$ to the surface. In addition, these waters have slightly lower salinities and thus lower
499 borate concentrations, which further diminish their buffering capacity, also reflected in the

500 high Revelle factors (Fig. 5a). For the same DIC value the buffering capacity of AAIW is
501 substantially lower than that of *u*CDW stemming from the low A_T of AAIW, which is also
502 reflected in the high ω DIC values. With the current calculated rate of increase of C_{ant} ,
503 aragonite will become under-saturated in AAIW around the year 2100, when DIC
504 concentrations reach $2208 \mu\text{mol kg}^{-1}$. This could happen even sooner, as wintertime, storm-
505 driven upwelling entrainment of deep waters into the surface in the SO is predicted to cause
506 seasonal aragonite under-saturation in the region as soon as 2030, when atmospheric CO_2
507 levels reach ~ 450 ppm (McNeil and Matear, 2008).

508

509 **5.4 Continued C_{ant} increase**

510 The buffering capacity of each water mass will be reduced by increasing the DIC
511 concentrations. To investigate how the buffering capacities of the different water masses in
512 this section have changed over time, and will continue to do so, the DIC buffer factors of
513 each water mass were calculated and plotted against DIC concentration (Fig. 6). Due to the
514 large relative error of the calculated ΔC_{ant} increases in the deeper waters, these were not
515 included. The high rate of uptake of C_{ant} by SACW means that this water mass has seen the
516 largest decrease in buffering capacity since pre-industrial times. The β DIC value has
517 decreased from 0.281 to 0.247 mmol kg^{-1} and Ω_{Ar} has decreased from 4.1 to 3.3. In contrast,
518 *u*CDW has shown relatively little change due to the low values of C_{ant} . However,
519 extrapolating our calculated C_{ant} rates of increase we predict a $33 \mu\text{mol kg}^{-1}$ increase in this
520 water mass over the next century, which will result in a significant reduction in buffering and
521 a pH decrease of -0.102. The buffering capacities of SAMW and AAIW follow a similar
522 pattern to each other, however, SAMW contains a greater proportion of subtropical water
523 than AAIW, thus it maintains a slightly higher buffering capacity than AAIW. Both AAIW
524 and *u*CDW will see a similar increase in C_{ant} over the next century (37 and $33 \mu\text{mol kg}^{-1}$,
525 respectively), however, the decline in Ω_{Ar} will be 1.6 times greater in AAIW, due to higher
526 ω DIC values. The SAMW will see approximately 54% of the increase in C_{ant} that SACW
527 will experience, however will undergo 84% of the associated pH decline. These extrapolated
528 predictions highlight the vulnerability of SAMW and AAIW to increasing C_{ant} , as also noted
529 by Gonzalez-Davila et al. (2011).

530

531 The observed pattern of ΔC_{ant} in the southwest Atlantic clearly identifies the SAZ as the most
532 effective entry point of C_{ant} into the ocean. In addition, the buffering factors of Egleston et al.
533 (2010) explicitly show that by the end of this century the two dominant water masses in this
534 area (SAMW and AAIW) will be the most sensitive to further C_{ant} increases. Whilst it is clear
535 that this will accelerate the rate of acidification in these water masses, it is unclear how it will
536 affect the CO_2 uptake in the SAZ. Assuming no changes to primary production, the increased
537 sensitivity of SAMW to DIC changes will lead to much greater seasonal variability in the
538 carbonate system of this water mass between the productive and non-productive period. The
539 biological uptake of DIC in the SAZ in austral spring and summer would lead to a more
540 dramatic decrease in surface water pCO_2 , allowing a greater air-sea pCO_2 flux. Conversely,
541 the acidification and decline in Ω_{Ar} may be detrimental to calcifying organisms in the area, as
542 observed in the Southern Ocean (Bednarsek et al., 2012), thus limiting export via the
543 biological pump.

544

545 The water masses SAMW and AAIW both risk further reduction in their buffering capacities
546 by long-term variability to their physical properties. On decadal time scales a freshening of
547 AAIW has been observed in the Pacific and Indian sectors of the Southern Ocean (Wong et
548 al., 1999). Decadal variability has also been noted in temperature, salinity and
549 biogeochemical parameters of SAMW (Bindoff et al., 2007; Alvarez et al., 2011), which
550 could further diminish or enhance the buffering capacity of this water mass and thus the C_{ant}
551 driven acidification. Variations on decadal time scales have been related to the Southern
552 Annular Mode, the dominant climate forcing over the region (Lovenduski et al., 2007;
553 Álvarez et al., 2011). Similarly in the North Atlantic, the North Atlantic Oscillation exerts a
554 degree of control over the carbonate system variables and C_{ant} uptake (Santana-Casiano et al.,
555 2007; Pérez et al., 2010). Such external controls will cause irregular C_{ant} uptake over time, as
556 has been observed by Brown et al. (2010), making it difficult to accurately predict future C_{ant}
557 uptake and associated changes in the buffering capacity.

558

559 **6 Conclusion**

560 The continuing uptake of C_{ant} in the southwest Atlantic has been assessed through application
561 of eMLR to two datasets collected in 1994 and 2011. The distribution of ΔC_{ant} is comparable
562 with previous studies of C_{ant} accumulation in the region (Ríos et al., 2010). The largest

563 increases are found in the SAZ, just north of the SAF; a previously identified substantial CO₂
564 sink (Metzl et al., 1999). The SACW (0.99±0.14 μmol kg⁻¹ y⁻¹), SAMW (0.53±0.11 μmol kg⁻¹
565 y⁻¹) and AAIW (0.36±0.06 μmol kg⁻¹ y⁻¹) are responsible for the greatest C_{ant} uptake,
566 consistent with earlier studies showing them to be an effective pathway of C_{ant} into the ocean
567 interior (Álvarez et al., 2009). The lower extent of AAIW demarks the greatest depth of
568 penetration of C_{ant} into the ocean in the past 17 years indicating that future uptake will,
569 similarly, be largely concentrated within the surface 1000m.

570

571 The increase in C_{ant} in the southwest Atlantic has led to acidification of water masses. The
572 calculated C_{ant}-driven acidification is greatest in SACW, where a current rate of pH decline
573 of 0.0016 yr⁻¹ is found. However, the acidification response per μmol kg⁻¹ increase in DIC is
574 greatest in the intermediate and mode waters. We identify SAMW as the water mass with the
575 greatest risk of rapid acidification in the future, due to a combination of its high C_{ant} uptake
576 and its limited buffering capacity. AAIW, on the other hand, is more at risk of aragonite
577 under-saturation due its low A_T values and resultant high ωDIC values. Continued increase of
578 C_{ant} at the current rate calculated will lead to aragonite under-saturation in the core of AAIW
579 around the year 2100.

580

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585

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844 Tables

845 Table 1a.

Min densi ty	Max densi ty	Mea n Lay er Dept h (m)	a	Si(O H) ₄	NO ₃	Sal	The ta	AO U	Pressu re	rms e	R ²	n
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	-0.35	1.36	26.14	-	0.57	-0.017	2.1	1.0	45
			6					3.38			0	
26.4	26.6	196	825	-0.35	3.68	36.18	-	0.23	0.003	2.4	1.0	72
								2.15			0	
26.6	26.8	259	124	-0.42	2.77	24.17	-	0.33	-0.004	1.7	1.0	67
			9					1.56			0	
26.8	27.0	310	111	-0.33	2.22	28.72	-	0.37	-0.012	1.6	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	-	0.16	-0.004	2.1	0.9	96
								3.07			9	
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	

Sigma-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						

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859 Table 1b.

Min densi ty	Max densi ty	Mea n Laye r Dept h (m)	a	Si(OH) ₄	NO 3	Sal	Thet a	AO U	Pressu re	rms e	R ²	n
<i>Sigma-θ</i>												
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		

Sigma-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	

						8							
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							

Sigma-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				7						

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863

864 **Table 2.**

Water	Density	Latitude	Pressure	dC_{ant}/dt	dC_{ant}/dt^a	dpH/dt
Mass	Range		(dbar)	($\mu\text{mol kg}^{-1}$ yr^{-1})	($\mu\text{mol kg}^{-1}$ yr^{-1})	(yr^{-1})
SACW	$\sigma^{\theta}20 -$ $\sigma^{\theta}26.8$	23°S - 18°S	90-160	0.99±0.14	0.90±0.04	-0.0016
SAMW	$\sigma^{\theta}26.8 -$ $\sigma^{\theta}27.1$	50°S - 48°S	90-160	0.53±0.11	0.53±0.02	-0.0014
AAIW	$\sigma^{\theta}27.1 -$ $\sigma^{\theta}27.4$	50°S - 48°S	360-450	0.36±0.06	0.36±0.06	-0.0010
<i>u</i>CDW	$\sigma^{\theta}27.4 -$ $\sigma^341.47$	50°S - 49°S	1400-1800	0.33±0.07	0.16±0.04	-0.0010
<i>u</i>NADW	$\sigma^{\theta}27.4 -$ $\sigma^341.47$	10°N - 15°N	1600-1800	0.20±0.03	0.16±0.04	-0.0005
<i>l</i>CDW	$\sigma^341.47 -$ $\sigma^445.9$	50°S - 48°S	3250-3750	0±0.06	0.08±0.04	0.0000
<i>l</i>NADW	$\sigma^341.47 -$ $\sigma^445.9$	10°N - 15°N	3000-3500	0±0.02	0.08±0.04	0.0000

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866

867 **Table 3.**

Water Mass	Salinity	Theta (°C)	γDIC (mmol kg⁻¹)	βDIC (mmol kg⁻¹)	ωDIC (mmol kg⁻¹)	Revelle Factor
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
<i>u</i>CDW	34.682	1.9528	0.132	0.143	-0.156	17.14
<i>u</i>NADW	34.987	3.8578	0.132	0.168	-0.191	14.40

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869

870 **Table Captions**

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

874

875 **Table 2.** The calculated rates of increase of C_{ant} and rates of decrease of pH along the section,
876 listed per water mass. The identification criteria for each water mass are provided. Error
877 represents $2\sigma/N^{0.5}$. ^aValues from Ríos et al. [2012].

878

879 **Table 3.** The average water mass values of salinity and potential temperature, with
880 accompanying average buffering capacity values (γ DIC, β DIC, ω DIC and Revelle factor)
881 calculated using the GEOTRACES-NL (2010/11) dataset. Water masses are determined
882 using the same criteria as given in Table 2.

883

884 **Figure Captions**

885 **Figure 1.** Stations where DIC and A_T samples were taken from both cruises (black
886 represents the WOCE '94 A17 stations, red represents the GEOTRACES-NL (2010/2011)
887 expeditions).

888

889 **Figure 2.** The residuals of the MLR fits of the (a) WOCE '94 A17 and (b) GEOTRACES-NL
890 (2010/2011) datasets.

891

892 **Figure 3.** Section distributions of temperature ($^{\circ}$ C), salinity, AOU ($\mu\text{mol kg}^{-1}$), silicate (μmol
893 kg^{-1}), A_T ($\mu\text{mol kg}^{-1}$) and DIC ($\mu\text{mol kg}^{-1}$) from the GEOTRACES-NL (2010/2011) dataset.

894

895 **Figure 4.** (a) Distribution of C_{ant} ($\mu\text{mol kg}^{-1}$) calculated using the φC_T^0 method with the
896 GEOTRACES-NL (2010/2011) dataset, (b) Distribution of $\Delta C_{\text{ant}}^{1994-2011}$ ($\mu\text{mol kg}^{-1}$),
897 calculated using the eMLR approach, (c) Distribution of the $\Delta\text{pH}^{1994-2011}$ associated with

898 $\Delta C_{\text{ant}}^{1994-2011}$. The aragonite saturation horizon (Ω_{Ar}) is marked on for pre-industrial times
899 (solid line), 1994 (dashed line) and 2011 (dotted line).

900

901 **Figure 5.** Distribution of the (a) Revelle factor across the section and the three buffering
902 factors relating to DIC; (b) β_{DIC} , (c) γ_{DIC} , and (d) ω_{DIC} . The latter three are all given in
903 mmol kg^{-1} .

904

905 **Figure 6.** The buffer factors β_{DIC} (top), γ_{DIC} (middle), and ω_{DIC} (bottom) of each water
906 mass over a range of DIC concentrations. The vertical lines denote the DIC concentration in
907 pre-industrial times, 1994, 2011 and the projected concentration in 2110.