

1 **Anthropogenic carbon inventory in the Gulf of Cádiz**

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15

16 **Abstract**

17

18 The North Atlantic is the most important sink for atmospheric CO₂ although there still
19 remain uncertainties about the total amount stored by this region and the contribution of
20 the anthropogenic CO₂ (C_{ANT}) that is exchanged between the Mediterranean Sea and the
21 Atlantic Ocean. During the P₃A₂ cruise performed in October 2008 throughout the
22 oceanic area covered by the Gulf of Cádiz and the Strait of Gibraltar, which channelizes
23 the water exchange between the Atlantic and the Mediterranean, extensive
24 measurements of the carbon system parameters (pH, total alkalinity and total inorganic
25 carbon) and others related (dissolved oxygen and nutrients) were carried out to analyse
26 their distribution in the area. In order to study the C_{ANT} spatial variability, three
27 observational methods for C_{ANT} concentration assessment (ϕC_T^o , ΔC^* and TrOCA)
28 were applied. The three water masses identified in the area, North Atlantic Central
29 Water (NACW), North Atlantic Deep Water (NADW) and Mediterranean Outflow
30 Water (MOW), were shown to contain different C_{ANT} concentration. NADW exhibited
31 the lowest C_{ANT} levels whereas NACW was the most C_{ANT} enriched. Data also indicate
32 a net import of C_{ANT} from the Atlantic towards the Mediterranean through Gibraltar.

33 Specific C_{ANT} inventories showed that MOW contributes in 8-12% to the total specific
34 C_{ANT} inventory of the Gulf of Cádiz.

35

36 **Keywords**

37

38 Anthropogenic CO_2 , Carbon storage, Water masses, Gulf of Cádiz, Strait of Gibraltar,
39 Mediterranean Sea.

40

41 **1. Introduction**

42

43 Since the late 18th Century, carbon dioxide (CO_2) concentration in the atmosphere has
44 been rising considerably, which is directly attributable to the fossil fuel burning and
45 changes in land use (deforestation, agriculture, etc.) by human activity (IPCC, 2007).
46 Nevertheless, atmospheric levels are lower than expected if all the CO_2 released by
47 anthropogenic sources had remained in the atmosphere. This mismatch is due to the fact
48 that the ocean and land biosphere have taken up a significant amount of CO_2 , thus
49 acting as sinks for the anthropogenic carbon dioxide (C_{ANT}) (Sarmiento and Gruber,
50 2002). It is known that the oceans represent the major of these two sinks, storing
51 approximately 48% of the total C_{ANT} (Sabine et al., 2004). Therefore, quantifying C_{ANT}
52 distribution and the total amount sequestered by the oceans is crucial to better
53 understand the role of the oceans in the global carbon cycle and how they moderate
54 climate change (IPCC, 2007). This analysis must be, however, conducted through
55 empirical methods based on the use of different tracers since C_{ANT} can not be directly
56 measured.

57

58 Several methods for the indirect estimation of C_{ANT} have been developed up to date.
59 Those based in the back-calculation technique (Brewer, 1978; Chen and Millero, 1979)
60 are quite extended as they were the first algorithms defined to assess the temporal
61 variation experienced by the measured inorganic carbon since a water mass was
62 originally formed. Such variation is due to the contribution of the organic matter
63 oxidation-reduction processes and the calcium carbonate dissolution-precipitation.
64 Gruber et al. (1996) improved the initial method that was developed for the Atlantic
65 Ocean and defined the quasi-conservative carbon tracer ΔC^* , which reflects the uptake

66 of C_{ANT} and the air-sea disequilibrium present when the water mass loses contact with
67 the atmosphere, assuming that it remains constant over time. A more recent method for
68 C_{ANT} computation is the TrOCA approach, which was originally proposed by Touratier
69 and Goyet (2004b) and further improved by Touratier et al (2007). This technique
70 considers a quasi-conservative tracer TrOCA, which combines Oxygen, inorganic
71 Carbon, and Total Alkalinity and that is based on the conservative NO tracer (Broecker,
72 1974; Ríos et al., 1989; Touratier and Goyet, 2004a). Both the TrOCA approach and the
73 ΔC^* technique assume that below the mixed layer, the decomposition of organic matter
74 follows a constant Redfield stoichiometry and that today's air-sea CO_2 disequilibrium is
75 identical to the one present in pre-industrial times. Current studies have indicated that
76 the TrOCA method considerably overestimates anthropogenic carbon concentrations
77 (Yool et al., 2011). Nevertheless, method has been still applied in our work in order to
78 compare the data obtained with the previous results shown by Ait-Ameur and Goyet
79 (2006) in the Gulf of Cádiz. A new parameterization , has been lately proposed by
80 Vazquez-Rodriguez et al. (2009a) , the so-called ϕC_T° method, which represents a
81 revision of ΔC^* and it is aimed at improving the assessment of C_{ANT} inventory in the
82 Atlantic Ocean. The main contribution of the ϕC_T° method is the use of sub-surface
83 layer data (100-200m) to reconstruct water mass formation conditions, thereby
84 obtaining better estimates of preformed properties instead of using other transient traces,
85 such as CFC, to quantify the effect of the air-sea disequilibrium on the C_{ANT}
86 concentration.

87

88 However, regardless of the method considered for C_{ANT} calculation, several studies
89 have confirmed that the North Atlantic is the most important sink for atmospheric CO_2
90 (Takahashi, 2009; Sabine et al., 2004), although there still remain uncertainties about
91 the total amount stored by this region. In the past, the contribution of areas such as
92 marginal seas, semi-enclosed seas and continental shelves to the global C_{ANT} inventories
93 was understudied. Nevertheless, recent studies that evaluate the CO_2 sink capacity of
94 these areas have demonstrated that they take up larger amounts of C_{ANT} which
95 contribute significantly to the overall global C_{ANT} inventories (Tanhua et al., 2009;
96 Schneider et al., 2010; Lee et al., 2011). Therefore, there is a clear research need to
97 accurately quantify the amount of carbon that is captured by the total coastal ocean and
98 subsequently transferred to the open sea. In response to this increasing interest, several
99 studies have been carried out in the coastal area comprised by the Gulf of Cádiz and the

100 Strait of Gibraltar (Aït-Ameur and Goyet, 2006; Huertas et al., 2006; 2009; de la Paz et
101 al., 2008, 2011; Ribas-Ribas et al., 2011). Data attained by these studies indicate that
102 this region acts as a moderate sink for atmospheric CO₂ and that a net export of total
103 inorganic carbon occurs from the Mediterranean to the Atlantic. On the other hand,
104 there have been contradicting results about the concentration of C_{ANT} that is exchanged
105 between both basins (Aït-Ameur and Goyet, 2006; Huertas et al., 2006; 2009). These
106 discrepancies may be related to the different methods used to obtain C_{ANT}
107 concentrations, as the TrOCA approach seems to overestimate Mediterranean waters
108 anthropogenic carbon levels. Therefore, the main aim of this work was to examine the
109 spatial variability of the C_{ANT} in the Gulf of Cádiz considering all the water masses
110 present in the area, in order to gain insights on the role of the Strait of Gibraltar in the
111 fluxes of the anthropogenic carbon. This analysis was performed by applying all the
112 aforementioned C_{ANT} calculation techniques not only with the aim at comparing the
113 results provided by the different methods currently available and generally applied but
114 also to allow the comparison with data reported in the past in this geographic zone by
115 using the TrOCA approach.. Furthermore, a C_{ANT} inventory for the whole area is
116 provided, with the relative contribution of the outflow of Mediterranean water to the
117 specific inventory being also given.

118

119 **1.1 Study Area**

120

121 The oceanic area covered by the Gulf of Cádiz and the Strait of Gibraltar, located
122 southwest of the Iberian Peninsula (Fig. 1), plays a relevant role in the general
123 circulation of the North Atlantic owing to the channelization of the water exchange
124 between the Atlantic and the Mediterranean Sea (Péliz et al., 2009; Criado-Aldeanueva
125 et al., 2009). Thus, the entrainment of North Atlantic Central Water (NACW) by the
126 Mediterranean outflow (MOW) as it descends the northern slope of the Gulf of Cádiz
127 markedly contributes to the generation of the Azores current and also drives upper slope
128 currents in the basin (Péliz et al., 2009).

129 The Strait of Gibraltar is a narrow and shallow channel with an east-west orientation of
130 a minimum width of 14 km (the Tarifa Narrows, TN in Fig. 1) and an average depth of
131 600 m, although the main sill of the Strait (Camarinal Sill, CS in Fig. 1) is hardly 300 m
132 depth and imposes a severe constrain for the ventilation of deep Mediterranean waters.
133 On the other hand, the adjacent Gulf of Cádiz is divided into two different portions by

134 Cape Santa Maria (CSM) (Fig. 1), with each of these halves presenting different
135 topographic characteristics. West of CSM, the continental shelf is narrow and the sea
136 bottom is characterized by the presence of submarine canyons. On the contrary, east of
137 the cape the continental shelf becomes wider and hosts important rivers whose mouths
138 provide the basin with freshwater and nutrients that control primary production in the
139 coastal fringe (Prieto et al., 2009). As underlined above, the circulation of water masses
140 in the Gulf is markedly controlled by the Mediterranean-Atlantic exchange that takes
141 place in the Strait of Gibraltar. The saltier and denser MOW moves westwards in depth,
142 being distinguishable through two main cores centred at about 800 and 1200 m depth.
143 This subdivision is probably due to the bottom topography that channels different
144 branches along certain isobaths (Ambar and Howe, 1979; Serra and Ambar, 2002). In
145 addition, a third shallower core can be detected at depths around 500 m in the
146 continental shelf (Ambar et al., 2002). In contrast, Atlantic waters flow eastward to the
147 Mediterranean Sea, occupying the upper layer in the Strait of Gibraltar. The confluence
148 of both water bodies determines the two layer circulation scheme found in the Strait.
149 The exchange of waters is mainly driven by the water deficit occurring in the
150 Mediterranean basin, as the excess of evaporation over precipitation and river run off
151 forces the Atlantic jet to progress towards the Mediterranean Sea to compensate water
152 losses (Bryden et al., 1994).

153 The presence of NACW in the area is evident below 100 m depth, as described in
154 previous studies (Navarro et al., 2006). This water mass has been categorized in two
155 varieties, such as the warmer Eastern North Atlantic Central Water of subtropical origin
156 (ENAC_t) and the colder subpolar Eastern North Atlantic Central Water (ENAC_s) (Ríos
157 et al., 1992; Pollard et al., 1996; Pérez et al., 2001; Alvarez et al., 2005). At shallower
158 depths, NACW is modified by the atmospheric interaction and it has been defined as
159 North Atlantic Surface Water (Gascard and Richez, 1985). Furthermore, the North
160 Atlantic Deep Water (NADW) can be found at depths greater than 1500 m (Emery and
161 Meincke, 1986; Alvarez et al., 2005) associated with a depth-decreasing thermohaline
162 properties (Ambar et al., 2002).

163

164 **2. Material and Methods**

165

166 **2.1. Sampling**

167

168 The P₃A₂ oceanographic cruise was conducted on board the R.V. Hespérides from the
169 04th to the 22nd of October 2008. A macroscale study was completed in a sampling grid
170 composed by 45 stations distributed from CSM to the Strait of Gibraltar (Fig.1). At each
171 station CTD profiles were obtained with a SeaBird SBE 911, followed by collection of
172 water samples with rosette at different depths (from 5 m up to ~2000 m or bottom
173 depth) in order to determine the spatial distribution of several biogeochemical variables,
174 such as total alkalinity, pH, dissolved oxygen and inorganic nutrients (nitrite, nitrate,
175 phosphate and silicate).

176

177 **2.2. Measurements**

178

179 **2.2.1. Total Alkalinity**

180

181 Total alkalinity (A_T) was measured with a Metrohm 794 Titroprocessor following the
182 method described by Mintrop et al. (2000). Water samples were taken from the Niskin
183 bottles and preserved in 500 mL borosilicate bottles poisoned with 100 µL of HgCl₂
184 saturated aqueous solution and kept until subsequent onboard and onshore analysis.
185 Accuracy of A_T determination was calculated from regular measurements of 2 batches
186 (batch # 85 and 89) of Certified Reference Material (CRM supplied by Prof. Andrew
187 Dickson, Scripps Institution of Oceanography, La Jolla, CA, USA), resulting in ±2
188 µmol kg⁻¹.

189

190 **2.2.2 pH**

191

192 pH was measured following the spectrophotometric method of Clayton and Byrne
193 (1993) using m-cresol purple as the indicator, and consequently, the scale used was the
194 total scale. Samples were collected directly from the rosette in 10 cm path-length optical
195 glass cells and measurements were carried out onboard with a Shimadzu UV-2401PC
196 spectrophotometer containing a 25°C-thermostated cells holder.

197 This method has been proved to have an accuracy of ±0.003 pH units (Clayton and
198 Byrne, 1993). Accuracy of our pH determinations was calculated from regular
199 measurements of 2 CRMs batches (# 85 and # 89). From both pH and A_T values, the
200 concentration of inorganic carbon (C_T) was calculated using the dissociation constants
201 from Mehrbach et al. (1973) refitted by Dickson and Millero (1987).

202

203 **2.2.3 Dissolved Oxygen**

204

205 Dissolved oxygen was determined following the Winkler method (Winkler, 1888).
206 Seawater was taken in sealed flasks directly from the Niskin bottles and stored in
207 darkness for at least 24 h. Analysis was performed by potentiometric determination
208 using a Metrohm 794 Titroprocessor, with an estimated error of $\pm 1 \mu\text{mol kg}^{-1}$.

209

210 **2.2.4 Nutrients**

211

212 Two 5 mL replicates of filtered seawater (GF/F Whatman filters) were taken and stored
213 at -20°C until onshore laboratory analysis. Concentration of NO_2 , NO_3 , PO_4 and Si
214 $(\text{OH})_4$ were obtained following the techniques described by Grasshoff et al. (1983) with
215 a Skalar San⁺⁺System autoanalyser.

216

217 **2.3. Calculation of C_{ANT} concentration**

218

219 As already indicated, several methods were applied to calculate C_{ANT} in the study
220 region: the TrOCA approach with the set of parameters proposed by Touratier and
221 Goyet (2004b) and with the latter improvements of Touratier et al. (2007), designated
222 here as TrOCA₂₀₀₄ and TrOCA₂₀₀₇ respectively; the back-calculation technique (ΔC^*)
223 and the ϕC_T° method. The original TrOCA₂₀₀₄ parameterization (Touratier and Goyet
224 2004b) was exclusively used to compare the results attained in this study with previous
225 estimations reported in the area based on such method (Aït-Ameur and Goyet, 2006).
226 Regardless of the calculation technique applied, the first 100 m of the water column
227 were excluded for C_{ANT} assessments and hence only data obtained in stations with
228 waters deeper than 100 m were considered.

229 C_{ANT} (TrOCA) has been computed using the following relationship

$$230 \quad C_{\text{ant}}(\text{TrOCA}_{2004;2007}) = \frac{\text{TrOCA} - \text{TrOCA}^\circ}{a}, \quad (2)$$

231 where TrOCA represents a semi-conservative tracer based on the Redfield oxidation-
232 reduction ratios of organic matter, calculated as follows:

$$233 \quad \text{TrOCA}_{2004} = \text{O}_2 + aC_T - 0.6A_T, \quad \text{TrOCA}_{2007} = \text{O}_2 + a(C_T - 1/2A_T), \quad (3, 4)$$

234 and TrOCA° is defined as the pre-industrial TrOCA:

235 $\text{TrOCA}^\circ_{2004} = 1505.04e^{(-\theta/89.04)}, \text{TrOCA}^\circ_{2007} = e^{(7.511+(1.087 \times 10^{-2})\theta - (7.81 \times 10^{-5}/A_T^2))}, \quad (5, 6)$

236 where the constant a is equal to 1.2 and 1.279 for the TrOCA_{2004} and the TrOCA_{2007}
 237 parameterizations respectively.

238

239 For the back-calculation technique, the following equation was used:

240 $C_{\text{ANT}}(\Delta C^*) = C_T - \text{AOU}/R_C - 1/2(\Delta A_T + \text{AOU}/R_N) - C_{T278}^\circ - \Delta C_{\text{dis}}, \quad (7)$

241 where C_T is the dissolved inorganic carbon concentration of the sample expressed in
 242 $\mu\text{mol kg}^{-1}$ and AOU stands for Apparent Oxygen Utilization, which was calculated
 243 using the oxygen saturation equation of Benson and Krause (1984). The stoichiometric
 244 coefficients R_C ($-\Delta\text{O}_2/\Delta\text{C}$) = 1.45 and R_N ($-\Delta\text{O}_2/\Delta\text{N}$) = 10.6 of Anderson and Sarmiento
 245 (1994) were taken. AOU/R_C corresponds to the C_T increase due to organic matter
 246 oxidation and $1/2(\Delta A_T + \text{AOU}/R_N)$ accounts for the C_T change due to CaCO_3 dissolution-
 247 precipitation, where $\Delta A_T = A_T - A_T^\circ$ is the total alkalinity variation since the water
 248 mass was formed. Preformed alkalinity (A_T°) and the disequilibrium term that stands
 249 for the air-sea CO_2 difference expressed in terms of C_T (ΔC_{dis}), were obtained for each
 250 water sample from the mixing proportion of the different water masses. This was carried
 251 out by an extended optimum multiparameter analysis (eOMP) (Poole and Tomczak,
 252 1999). The A_T° type values for the Atlantic Waters were calculated using the approach
 253 proposed by Perez et al. (2002) while those by Rhein and Hinrichsen (1993) and
 254 Santana-Casiano et al. (2002) were used for the MOW. C_{T278}° represents the C_T in
 255 equilibrium with the preindustrial atmospheric CO_2 molar fraction of 278 ppm and was
 256 calculated using the dissociation constants of Merbach et al. (1973) refitted by Dickson
 257 and Millero (1987). ΔC_{dis} for both NACW and NADW was considered to be -12 ± 5
 258 $\mu\text{mol kg}^{-1}$ and $-10 \pm 8 \mu\text{mol kg}^{-1}$, respectively (Lee et al. 2003) whereas for the MOW
 259 ΔC_{dis} was obtained from Huertas et al. (2009), which sets ΔC_{dis} in $0 \pm 5 \mu\text{mol kg}^{-1}$ using
 260 the CFC data given by Rhein and Hinrichsen (1993). As for the ϕC_T° method (Vazquez-
 261 Rodriguez et al. 2009a), new A_T° and ΔC_{dis} parameterizations were included in the
 262 equation based on a 100-200 m depth surface layer that is taken as a reference for
 263 reconstructing water mass formation conditions. Accordingly, the NO and PO
 264 conservative tracers defined by Broecker (1974) and the preformed silicate (S_i°)
 265 provided by Perez et al. (2002) were used. For the term ΔC_{dis} , a distinction depending
 266 on different potential temperature (θ) intervals was made in the case of Atlantic waters

267 whereas for the MOW ($S > 36.5$), A_T° and ΔC_{dis} were obtained by eOMP analysis. The
 268 different water masses found in the area were defined in the eOMP analysis by several
 269 water types (WT): WT1 and WT2 correspond to the two different varieties of NACW
 270 (ENACWt and ENACWs, respectively), WT3 designates NADW and WT4 marks MOW,
 271 as summarized in Table 1.

272

273 Therefore, the C_{ANT}° calculation equation can be summarized as follows

$$274 \quad C_{\text{ANT}}(\varphi C_T^0) = \frac{\Delta C^* - \Delta C_{\text{dis}}^t}{1 + \varphi \left| \Delta C_{\text{dis}}^t \right| / C_{\text{ant}}^{\text{sat}}}, \quad (8)$$

275 with $\Delta C^* = C_T - \text{AOU}/R_C - \Delta \text{Ca} - C_{\text{T278}}^\circ$ where ΔCa is the term related to the CaCO_3
 276 dissolution, since $\Delta \text{Ca} = 0.5(\text{PA}_{\text{T,observed}} - \text{PA}_T^\circ)$ with $\text{PA}_T = A_T + \text{NO}_3 + \text{PO}_4$ and
 277 $\text{PA}_T^\circ = A_T^\circ + \text{NO}_3^\circ + \text{PO}_4^\circ$, being $\text{NO}_3^\circ = \text{NO}_3 - \text{AOU}/9$ and $\text{PO}_4^\circ = \text{PO}_4 - \text{AOU}/135$.
 278 The $\text{O}_2:\text{N}=9$ and $\text{O}_2:\text{P}=135$ Redfield ratios proposed by Broecker (1974) were taken.
 279 Furthermore, in the $C_{\text{ANT}}(\varphi C_T^0)$ equation, the constant term φ is a proportionality
 280 factor and equals the ratio between the temporal variability of the air-sea disequilibrium
 281 of CO_2 from the time of pre-industrial water mass formation to the time “t” ($\Delta \Delta C_{\text{dis}}$),
 282 with the disequilibrium at the time “t” being ΔC_{dis}^t . Finally, $C_{\text{ant}}^{\text{sat}}$ represents the
 283 anthropogenic carbon saturation referred to a $x\text{CO}_2$ air of 384 ppm, which is taken from
 284 measurements performed at the meteorological station of the Lampedusa (Italy,
 285 Cooperative Air Sampling Network of the NOAA/ESRL Global Monitoring Division)
 286 and it is included to account for the effects of temperature and salinity on the solubility
 287 of C_{ANT} in the different water masses.

288 In order to estimate the uncertainty associated to the C_{ANT} calculation techniques an
 289 error propagation analysis was conducted for each method. The error for C_{ANT}
 290 assessments using the TrOCA₂₀₀₄ and the TrOCA₂₀₀₇ parameterizations were $\pm 5.3 \mu\text{mol}$
 291 kg^{-1} and $\pm 5.5 \mu\text{mol kg}^{-1}$, respectively; $\pm 6.1 \mu\text{mol kg}^{-1}$ when the ΔC^* technique was
 292 applied and $\pm 5.6 \mu\text{mol kg}^{-1}$ in the case of the φC_T° method. In previous works, the
 293 overall estimated C_{ANT} uncertainties ranged from ± 3 to $5.9 \mu\text{mol kg}^{-1}$ for the TrOCA₂₀₀₄
 294 approach (Touratier et al. 2004b), ± 6.2 for the TrOCA₂₀₀₇ parameterization (Touratier et
 295 al. 2007), ± 9 for the ΔC^* technique (Gruber et al. 1996) and ± 5.2 for the φC_T° method
 296 (Vazquez-Rodriguez et al. 2009a).

297

298 **3. Results and Discussion**

299

300 **3.1. Water masses and carbon system parameters in the study area.**

301

302 Three water masses were clearly identified in the Gulf of Cádiz according to their
303 different thermohaline properties (Fig.2a): NACW, NADW and MOW. NACW, located
304 above 500 m depth, was well defined with a temperature range from 11 to 18 °C and
305 salinity values around 35.5-36.3. This water mass showed a linear behaviour for the
306 isopycnals interval of $26.6 \text{ kg m}^{-3} \leq \sigma_{\theta} \leq 27.3 \text{ kg m}^{-3}$, as described in Criado-Aldeanueva
307 et al. (2006). The MOW signal could be detected throughout the entire study area and
308 up to 1500 m depth (Figs. 5f, 6f). In particular, MOW in the Strait of Gibraltar is
309 defined by a salinity of 38.5 and a temperature value of 13°C (Figs. 4b-c) (Gascard and
310 Richez 1985; Garcia-Lafuente et al. (2007) whereas in the Gulf of Cadiz was clearly
311 evident at a pressure of around 1000 dbar because of a salinity and potential temperature
312 increase (Fig. 3b-c). This signal corresponds to the lower core of the MOW (Fig. 5f)
313 (Ambar and Howe, 1979; Serra and Ambar, 2002). In contrast, NADW was found in a
314 reduced number of deep stations (depth>1500 m) located in the southwestern part of the
315 surveyed region (Fig. 5e, 6e). This water mass was previously described in the Iberian
316 Basin by Alvarez et al. (2005) with salinity and temperature values around 34.9 and 2.4
317 °C, respectively. In our study, NADW was slightly modified as it showed salinity and
318 temperature values around 35°C and 5°C respectively (Figs. 3b-c, 4b-c).

319 All the water masses identified were also characterized by specific carbonate properties,
320 as the variability of A_T , AOU and C_T (Figs. 2b-d) was well correlated with the
321 distribution of the different water masses. Due to the shallower location of the NACW
322 (Figs. 5d, 6d), its thermohaline properties suffer modifications caused by the air-sea
323 interactions and river discharges (Criado-Aldeanueva et al., 2009), which resulted in the
324 highest variability found for these parameters within the same water mass (Figs. 2b-d).
325 Moreover, the pattern of AOU allowed to distinguish the presence of the two varieties
326 of the NACW described in the area: the ENAC_t, which is oxygen saturated, was thereby
327 characterized by the lowest AOU levels at about $6 \mu\text{mol kg}^{-1}$ (Fig. 2c), coinciding with
328 previous reports (Ait-Ameur and Goyet, 2006) and the ENAC_s, which is located below
329 the former, and exhibited an increase in the AOU levels (Fig. 2c). Perez et al. (2001)

330 attributed this deeper AOU maximum to the remineralization of organic matter in the
331 African coast linked to the northwest African upwelling system. Within the NACW
332 layer, A_T and C_T showed intermediate levels in relation to the total measurements, with
333 average values around 2360 ± 2 and $2130 \pm 2 \mu\text{mol kg}^{-1}$, respectively (Figs. 2b,d, 3d-e, 4d-
334 e). As expected, the highest A_T ($2576 \pm 6 \mu\text{mol kg}^{-1}$) and C_T contents ($2317 \pm 5 \mu\text{mol kg}^{-1}$)
335 ¹) were found in the MOW located in the western side of the Strait (Figs. 2b-d). In the
336 vertical sections of the N-S and W-E transects, the biogeochemical properties of the
337 MOW were also evident in the lower core (Figs. 3d-f, 5f) and in the western part of the
338 Strait (Figs. 4d-f, 6f), with values that coincide with those reported by Aït-Ameur and
339 Goyet (2006) and Huertas et al. (2009) in the area. The elevated AOU levels of about 80
340 $\mu\text{mol kg}^{-1}$ within this layer indicated the lower oxygen concentrations present in the
341 MOW due to the active remineralisation of organic matter occurring in the
342 Mediterranean basin (Huertas et al., 2009).

343 On the other hand, the A_T and C_T signatures inside the NADW showed lower values
344 equivalent to $2329 \pm 7 \mu\text{mol kg}^{-1}$ and $2167 \pm 2 \mu\text{mol kg}^{-1}$, respectively (Fig. 2b, d). In fact,
345 data plotted in the vertical sections of the transects revealed a decrease of these
346 properties with depth (Figs. 3d-e, 4d-e) due to the presence of this water mass (Figs. 5e,
347 6e). It is also worth mentioning that the high AOU values ($\sim 80 \mu\text{mol kg}^{-1}$) detected in
348 this water mass (Fig. 2c) can be related to the ageing of water masses that results in a
349 simultaneous increase in AOU, nitrate and phosphate owing to the mineralization of
350 organic matter (van Aken, 2000).

351

352 The linear relationship between salinity and A_T obtained for the whole region was
353 calculated at a salinity reference of 35 in order to remove spatio-temporal changes. The
354 equation obtained ($A_T = [(84.3 \pm 1.6) * (S - 35) - (2277 \pm 2)]$, $r^2 = 0.95$, $n = 156$) indicated that
355 mixing is the main controlling factor for the A_T distribution, in a similar way as in
356 Santana-Casiano et al., (2002) and Huertas et al., (2009). These authors reported linear
357 relationships of $A_T = 2353 (\pm 0.4) + 92.28 (\pm 0.31) (S - 36.0)$ ($r^2 = 0.998$) and $A_T = 92.98 \times S -$
358 993 ($r^2 = 0.989$) for the Gulf and the Strait, respectively. The new relationship attained
359 here was based on data collected in a wider area, which is influenced by the presence of
360 water masses with lower salinity, such as the NADW, which is absent in the Strait. This
361 circumstance may explain the reduction in the slope and the slight diminution in the
362 correlation coefficient compared to the ones reported by previous works.

363

364 3.2. C_{ANT} distribution

365

366 The vertical distribution of C_{ANT} calculated using the TrOCA₂₀₀₇, the ΔC^* and the ϕC_T°
367 methods is plotted in Fig. 5 for a N-S section and in Fig. 6 for an E-W section. The red
368 transects indicated in Figs. 3a and 4a were chosen as representatives of all the legs
369 sampled.

370 In the N-S section, the spatial pattern of C_{ANT} was similar regardless of the method used
371 for computation, as all of them resulted in a vertical decreasing gradient (Figs. 5a-c).
372 The maximum concentrations of C_{ANT} were consistently located in 100 m depth waters
373 ($50\text{-}60 \mu\text{mol kg}^{-1}$), where the highest proportion of NACW was present (Fig. 5d). In
374 contrast, the lowest C_{ANT} values were found at depths below 1500 dbar (Figs. 5a-c) due
375 to the slight C_{ANT} penetration into the domain of the NADW (Fig. 5e), as described by
376 Ríos et al., 2001). Within this layer, C_{ANT} concentrations showed concordant values
377 between 9 and $12 \mu\text{mol kg}^{-1}$ for all the methods applied (Figs. 5a-c). The higher salinity
378 zone found at about 1000-1200 dbar in the continental slope (Fig. 3b) and
379 corresponding to the lower MOW core (Fig. 5f), was characterized by an increase in
380 C_{ANT} concentration, especially when the TrOCA₂₀₀₇ parameterization was used (Fig.
381 5c), resulting in concentrations of $50 \mu\text{mol kg}^{-1}$ approximately.

382

383 In the E-W section, the distribution of C_{ANT} (Figs. 6a-c) revealed a similar trend for the
384 three parameterizations used except for that obtained in the Strait of Gibraltar with the
385 TrOCA₂₀₀₇ approach. According to this method, the MOW located in the Strait was
386 characterised by the highest C_{ANT} content (Fig.6c), particularly waters with salinities
387 >37.5 (Fig.4b). C_{ANT} TrOCA₂₀₀₇ concentration in the easternmost part displayed values
388 around $63 \pm 1 \mu\text{mol kg}^{-1}$ (Fig.6c), which declined westwards and upwards in the water
389 column. Moreover, when the original TrOCA₂₀₀₄ parameterization was applied in order
390 to compare with previous estimates (not shown), MOW exhibited average C_{ANT} levels
391 of $92 \pm 1 \mu\text{mol kg}^{-1}$, whereas NADW and NACW showed $24 \pm 4 \mu\text{mol kg}^{-1}$ and 55 ± 1
392 $\mu\text{mol kg}^{-1}$ in good agreement with the values reported by Ait-Ameur et al. (2006).
393 Therefore, comparing both TrOCA parameterizations, the initial TrOCA₂₀₀₄ method
394 yielded values around 40% higher than those attained by the technique subsequently
395 refined (Fig. 6c).

396 On the contrary, when both the ϕC_T° and ΔC^* methods were applied in the Strait, higher
397 C_{ANT} concentrations were detected within the NACW located in the upper layer of the

398 water column, with a decreasing vertical pattern being also evidenced (Figs. 6a, c). This
399 discrepancy can be explained by the nature of the equations, as the general TrOCA
400 approach applies a global formula that is a function exclusively of θ , O_2 and A_T
401 measured *in situ* (Eqs. 3, 4) whereas the back-calculation techniques include the
402 computation of the pre-industrial carbon level and the disequilibrium due to the air-sea
403 CO_2 difference (Eqs. 5, 6), which are adapted regionally considering the formation of
404 each particular water mass. This feature was already highlighted in the early analysis
405 performed in the Strait by Huertas et al., (2009). In the rest of the surveyed region, the
406 ranges of C_{ANT} concentration within the NACW and NADW coincide with those
407 observed in the N-S transect independent of the approach applied.

408

409 **3.3. C_{ANT} inventory**

410

411 The specific inventory of C_{ANT} for the entire area was determined by integrating the
412 average vertical C_{ANT} profiles attained at each station from surface down to the bottom
413 depth. Because C_{ANT} concentrations were calculated from 100 dbar to the sea bottom,
414 the surface layer above this depth was assumed to contain a constant C_{ANT} level equal to
415 that present at this upper limit, which also marks the winter mixing layer for Atlantic
416 subtropical waters (Vázquez-Rodríguez et al., 2009a). This artefact for inventory
417 computations allows to avoid the influence of the seasonal biogeochemical variability
418 on surface C_{ANT} estimates (Lo Monaco et al., 2005; Vázquez-Rodríguez et al., 2009a).
419 Specific inventories calculated in the region by the different techniques showed small
420 differences (Table 2). Nevertheless, should be taken into account in the inventory results
421 obtained that they represent average values for the totality of the waters masses present
422 in the area (not shown). As is shown in the Table 2, the initial TrOCA₂₀₀₄ method
423 yielded the highest specific inventory with $38.0 \pm 3.1 \text{ mol C m}^{-2}$, whereas the rest of
424 calculation techniques resulted in similar values, with the minimum provided by the
425 ϕC_T° method equivalent to $33.5 \pm 3.2 \text{ mol C m}^{-2}$. Estimates were statistically analyzed
426 by a student's t test and averaged results obtained showed no statistical differences
427 between the different methods applied.

428

429 These values are comparable to the specific inventory presented by Lee et al. (2011) for
430 the East/Japan Sea and equal to $34 \pm 5.1 \text{ mol C m}^{-2}$. The specific inventory for the entire
431 Eastern North Atlantic comprised in the 30°N-40°N latitude band, where our study area

432 is contained, has been estimated in $66.2 \text{ mol C m}^{-2}$, using the ΔC^* (Lee et al., 2003) and
433 in 75 mol C m^{-2} with the ϕC_T° method (Vázquez-Rodríguez et al., 2009b) . The
434 differences between such estimates and those obtained here are due to the lower volume
435 of water contained in the surveyed region in relation to that of the Eastern North
436 Atlantic, as the vertical interpolation markedly depends of the water column volume.

437

438 Since the main differences in the C_{ANT} contents observed in our study were related to
439 the presence of the Mediterranean waters (Figs. 6a-c), the contribution of the MOW to
440 the specific C_{ANT} inventory was also calculated with each technique. Results
441 summarized in Table 2 indicate that the Mediterranean supplies 8% of the total C_{ANT}
442 specific inventory when the ϕC_T° and ΔC^* methods were used. A small increase in this
443 contribution (11-12 %) was attained with the two TrOCA approaches, as a result of the
444 higher concentration of C_{ANT} assigned to the MOW by both parameterizations (Fig. 6c).

445

446 **4. Conclusions**

447

448 The analysis of the spatial distribution of the carbon system parameters in the area
449 covered by the Gulf of Cádiz and the Strait of Gibraltar reflected the presence of
450 different water masses that were characterized by distinct biogeochemical properties.
451 The concentration of C_{ANT} calculated for each water mass according to three estimation
452 methods resulted in small variations. The main discrepancies between the results
453 obtained by all the methods were found in the MOW, as both TrOCA approaches seem
454 to overestimate C_{ANT} concentration within this water mass. Accordingly, slight
455 differences were found in the specific inventories with the exception of the value
456 provided by the TrOCA₂₀₀₄ approach. Furthermore, the quantification of the additive
457 effect of the C_{ANT} contained in the MOW on that measured in Atlantic waters at
458 intermediate depths has been evidenced in this study. This work also presents new data
459 on the C_{ANT} levels present in a coastal ocean region, whose role in the capture and
460 storage of CO_2 had been underestimated in the past. These results also represent a
461 contribution to the North Atlantic specific carbon inventories.

462

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470

471 **6. References**

472

473 Ait-Ameur, N., Goyet, C., 2006. Distribution and transport of natural and anthropogenic
474 CO₂ in the Gulf of Cadiz. Deep-Sea Research Part II-Topical Studies in Oceanography
475 53, 1329-1343

476 Alvarez, M., Perez, F.F., Shoosmith, D.R., Bryden, H.L., 2005. Unaccounted role of
477 Mediterranean Water in the drawdown of anthropogenic carbon. Journal of Geophysical
478 Research-Oceans 110

479 Ambar, I., Howe, M.R., 1979. Observations of the Mediterranean Outflow .2. Deep
480 circulation in the vicinity of the Gulf of Cadiz. Deep-Sea Research-Part I-
481 Oceanographic Research Papers 26, 555-568

482 Ambar, I., Serra, N., Brogueira, M.J., Cabecadas, G., Abrantes, F., Freitas, P.,
483 Goncalves, C., Gonzalez, N., 2002. Physical, chemical and sedimentological aspects of
484 the Mediterranean outflow off Iberia. Deep-Sea Research Part II-Topical Studies in
485 Oceanography 49, 4163-4177

486 Anderson, L.A., Sarmiento, J.L., 1994. Redfield ratios of remineralization determined
487 by nutrient data analysis. Global Biogeochemical Cycles 8, 65-80

488 Benson, B.B., Krause, D., 1984. The concentration and isotopic fractionation of oxygen
489 dissolved in fresh-water and seawater in equilibrium with the atmosphere. Limnology
490 and Oceanography 29, 620-632

491 Brewer, P.G., 1978. Direct observation of oceanic CO₂ increase. Geophysical Research
492 Letters 5, 997-1000

493 Broecker, W.S., 1974. NO a conservative water-mass tracer. Earth and Planetary
494 Science Letters 23, 100-107

495 Bryden, H.L., Candela, J., Kinder, T.H., 1994. Exchange through the Strait of Gibraltar.
496 Progress in Oceanography 33, 201-248

497 Clayton, T.D., Byrne, R.H., 1993. Spectrophotometric seawater pH measurements- total
498 hydrogen scale calibration of m-cresol purple ant at-sea results. Deep-Sea Research Part
499 I-Oceanographic Research Papers 40, 2115-2129

500 Criado-Aldeanueva, F., Garcia-Lafuente, J., Navarro, G., Ruiz, J., 2009. Seasonal and
501 interannual variability of the surface circulation in the eastern Gulf of Cadiz (SW
502 Iberia). *Journal of Geophysical Research-Oceans* 114

503 Criado-Aldeanueva, F., Garcia-Lafuente, J., Vargas, J.M., Del Rio, J., Vazquez, A.,
504 Reul, A., Sanchez, A., 2006. Distribution and circulation of water masses in the Gulf of
505 Cadiz from in situ observations. *Deep-Sea Research Part II-Topical Studies in*
506 *Oceanography* 53, 1144-1160

507 Chen, C.T., Millero, F.J., 1979. Gradual increase of oceanic carbon dioxide. *Nature* 277,
508 205-206

509 de la Paz, M., Debelius, B., Macias, D., Vazquez, A., Gomez-Parra, A., Forja, J.M.,
510 2008. Tidal-induced inorganic carbon dynamics in the Strait of Gibraltar. *Continental*
511 *Shelf Research* 28, 1827-1837

512 de la Paz, M., Huertas, M.E., Padín, X.-A., González-Dávila, M., Santana-Casiano, M.,
513 Forja, J.M., Orbi, A., Pérez, F.F., Ríos, A.F., 2011. Reconstruction of the seasonal cycle
514 of air-sea CO₂ fluxes in the Strait of Gibraltar. *Marine Chemistry* In Press, Corrected
515 Proof

516 Dickson, A.G., Millero, F.J., 1987. A comparison of the equilibrium-constants for the
517 dissociation of carbonic-acid in seawater media. *Deep-Sea Research Part I-*
518 *Oceanographic Research Papers* 34, 1733-1743

519 Emery, W.J., Meincke, J., 1986. *Global Water Masses - Summary and Review.*
520 *Oceanologica Acta* 9, 383-391

521 Garcia-Lafuente, J., Roman, A.S., del Rio, G.D., Sannino, G., Garrido, J.C.S., 2007.
522 Recent observations of seasonal variability of the Mediterranean outflow in the Strait of
523 Gibraltar. *Journal of Geophysical Research-Oceans* 112

524 Gascard, J.C., Richez, C., 1985. Water masses and circulation in the Western Alboran
525 Sea and in the Strait of Gibraltar. *Progress in Oceanography* 15, 157-216

526 Grasshoff, K., Ehrhard, M., Kremling, K., 1983. Determination of nutrients. In:
527 *Methods of Seawater Analysis*, 2nd ed. Verlag Chemie, Weinheim.

528 Gruber, N., Sarmiento, J.L., Stocker, T.F., 1996. An improved method for detecting
529 anthropogenic CO₂ in the oceans. *Global Biogeochemical Cycles* 10, 809-837

530 Huertas, I.E., Navarro, G., Rodriguez-Galvez, S., Lubian, L.M., 2006. Temporal
531 patterns of carbon dioxide in relation to hydrological conditions and primary production
532 in the northeastern shelf of the Gulf of Cadiz (SW Spain). *Deep-Sea Research Part II-*
533 *Topical Studies in Oceanography* 53, 1344-1362

534 Huertas, I.E., Rios, A.F., Garcia-Lafuente, J., Makaoui, A., Rodriguez-Galvez, S.,
535 Sanchez-Roman, A., Orbi, A., Ruiz, J., Perez, F.F., 2009. Anthropogenic and natural
536 CO₂ exchange through the Strait of Gibraltar. *Biogeosciences* 6, 647-662

537 IPCC, 2007. *Climate Change 2007: The Physical Science Basis*, Contribution of
538 Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on
539 Climate Change. Cambridge University Press, Cambridge, United Kingdom. New York,
540 NY, USA.

541 Lee, K., Choi, S.D., Park, G.H., Wanninkhof, R., Peng, T.H., Key, R.M., Sabine, C.L.,
542 Feely, R.A., Bullister, J.L., Millero, F.J., Kozyr, A., 2003. An updated anthropogenic
543 CO₂ inventory in the Atlantic ocean. *Global Biogeochemical Cycles* 17

544 Lee, K., Sabine, C.L., Tanhua, T., Kim, T.W., Feely, R.A., Kim, H.C., 2011. Roles of
545 marginal seas in absorbing and storing fossil fuel CO₂. *Energy & Environmental*
546 *Science* 4, 1133-1146

547 Lo Monaco, C., Goyet, C., Metzl, N., Poisson, A., Touratier, F., 2005. Distribution and
548 inventory of anthropogenic CO₂ in the Southern Ocean: Comparison of three data-based
549 methods. *Journal of Geophysical Research-Oceans* 110

550 Mehrbach, C., Culberso, Ch, Hawley, J.E., Pytkowic, Rm, 1973. Measurements of
551 apparent dissociation-constants of carbonic-acid in seawater at atmospheric-pressure.
552 *Limnology and Oceanography* 18, 897-907

553 Mintrop, L., Perez, F.F., Gonzalez-Davila, M., Santana-Casiano, M.J., Kortzinger, A.,
554 2000. Alkalinity determination by potentiometry: Intercalibration using three different
555 methods. *Ciencias Marinas* 26, 23-37

556 Navarro, G., Ruiz, J., Huertas, I.E., Garcia, C.M., Criado-Aldeanueva, F., Echevarria,
557 F., 2006. Basin-scale structures governing the position of the deep fluorescence
558 maximum in the Gulf of Cadiz. *Deep-Sea Research Part II-Topical Studies in*
559 *Oceanography* 53, 1261-1281

560 Péliz, A., Marchesiello, P., Santos, A.M.P., Dubert, J., Teles-Machado, A., Marta-
561 Almeida, M., Le Cann, B., 2009. Surface circulation in the Gulf of Cadiz: 2. Inflow-
562 outflow coupling and the Gulf of Cadiz slope current. *Journal of Geophysical Research-*
563 *Oceans* 114

564 Pérez, F.F., Álvarez, M., Ríos, A.F., 2002. Improvements on the back-calculation
565 technique for estimating anthropogenic CO₂. *Deep-Sea Research Part I-Oceanographic*
566 *Research Papers* 49, 859-875

567 Pérez, F.F., Mintrop, L., Llinas, O., González-Davila, M., Castro, C.G., Alvarez, M.,
568 Kortzinger, A., Santana-Casiano, M., Rueda, M.J., Ríos, A.F., 2001. Mixing analysis of
569 nutrients, oxygen and inorganic carbon in the Canary Islands region. *Journal of Marine*
570 *Systems* 28, 183-201

571 Pollard, R.T., Griffiths, M.J., Cunningham, S.A., Read, J.F., Perez, F.F., Rios, A.F.,
572 1996. Vivaldi 1991-A study of the formation, circulation and ventilation of Eastern
573 North Atlantic Central Water. *Progress in Oceanography* 37, 167-192

574 Poole, R., Tomczak, M., 1999. Optimum multiparameter analysis of the water mass
575 structure in the Atlantic Ocean thermocline. *Deep-Sea Research Part I-Oceanographic*
576 *Research Papers* 46, 1895-1921

577 Prieto, L., Navarro, G., Rodriguez-Galvez, S., Huertas, I.E., Naranjo, J.M., Ruiz, J.,
578 2009. Oceanographic and meteorological forcing of the pelagic ecosystem on the Gulf
579 of Cadiz shelf (SW Iberian Peninsula). *Continental Shelf Research* 29, 2122-2137

580 Rhein, M., Hinrichsen, H.H., 1993. Modification of Mediterranean Water in the Gulf of
581 Cadiz, studied with hydrographic, nutrient and chlorofluoromethane data. *Deep-Sea*
582 *Research Part I-Oceanographic Research Papers* 40, 267-291

583 Ribas-Ribas, M., Gómez-Parra, A., Forja, J.M., 2011. Air-sea CO₂ fluxes in the north-
584 eastern shelf of the Gulf of Cádiz (southwest Iberian Peninsula). *Marine Chemistry* 123,
585 56-66

586 Ríos, A.F., Fraga, F., Pérez, F.F., 1989. Estimation of coefficients for the calculation of
587 "NO", "PO" and "CO", starting from the elemental composition of natural
588 phytoplankton*. *Scientia Marina* 53, 779-784

589 Ríos, A.F., Pérez, F.F., Fraga, F., 1992. Water masses in the upper and middle North-
590 Atlantic Ocean East of the Azores. *Deep-Sea Research Part I-Oceanographic Research*
591 *Papers* 39, 645-658

592 Ríos, A.F., Pérez, F.F., Fraga, F., 2001. Long-term (1977-1997) measurements of
593 carbon dioxide in the Eastern North Atlantic: evaluation of anthropogenic input. *Deep-*
594 *Sea Research Part II-Topical Studies in Oceanography* 48, 2227-2239

595 Sabine, C.L., Feely, R.A., Gruber, N., Key, R.M., Lee, K., Bullister, J.L., Wanninkhof,
596 R., Wong, C.S., Wallace, D.W.R., Tilbrook, B., Millero, F.J., Peng, T.H., Kozyr, A.,
597 Ono, T., Rios, A.F., 2004. The oceanic sink for anthropogenic CO₂. *Science* 305, 367-
598 371

599 Santana-Casiano, J.M., González-Davila, M., Laglera, L.M., 2002. The carbon dioxide
600 system in the Strait of Gibraltar. *Deep-Sea Research Part II-Topical Studies in*
601 *Oceanography* 49, 4145-4161

602 Sarmiento, J.L., Gruber, N., 2002. Sinks for anthropogenic carbon. *Physics Today* 55,
603 30-36

604 Schneider, A., Tanhua, T., Körtzinger, A., Wallace, D.W.R., 2010. High anthropogenic
605 carbon content in the eastern Mediterranean. *Journal of Geophysical Research-Oceans*
606 115, 11

607 Serra, N., Ambar, I., 2002. Eddy generation in the Mediterranean undercurrent. *Deep-*
608 *Sea Research Part II-Topical Studies in Oceanography* 49, 4225-4243

609 Takahashi, T., 2009. Climatological mean and decadal change in surface ocean pCO₂,
610 and net sea-air CO₂ flux over the global oceans. *Deep-Sea Research Part II-Topical*
611 *Studies in Oceanography* 56, 554-577

612 Tanhua, T., Jones, E.P., Jeansson, E., Jutterstrom, S., Smethie, W.M., Wallace, D.W.R.,
613 Anderson, L.G., 2009. Ventilation of the Arctic Ocean: Mean ages and inventories of
614 anthropogenic CO₂ and CFC-11. *Journal of Geophysical Research-Oceans* 114

615 Touratier, F., Azouzi, L., Goyet, C., 2007. CFC-11, Delta C-14 and H-3 tracers as a
616 means to assess anthropogenic CO₂ concentrations in the ocean. *Tellus Series B-*
617 *Chemical and Physical Meteorology* 59, 318-325

618 Touratier, F., Goyet, C., 2004a. Definition, properties, and Atlantic Ocean distribution
619 of the new tracer TrOCA. *Journal of Marine Systems* 46, 169-179

620 Touratier, F., Goyet, C., 2004b. Applying the new TrOCA approach to assess the
621 distribution of anthropogenic CO₂ in the Atlantic Ocean. *Journal of Marine Systems* 46,
622 181-197

623 van Aken, H.M., 2000. The hydrography of the mid-latitude northeast Atlantic Ocean I:
624 The deep water masses. *Deep-Sea Research Part I-Oceanographic Research Papers* 47,
625 757-788

626 Vázquez-Rodríguez, M., Padín, X.A., Ríos, A.F., Bellerby, R.G.J., Pérez, F.F., 2009a.
627 An upgraded carbon-based method to estimate the anthropogenic fraction of dissolved
628 CO₂ in the Atlantic Ocean. *Biogeosciences Discussions* 6, 4527-4571

629 Vázquez-Rodríguez, M., Touratier, F., Lo Monaco, C., Waugh, D.W., Padín, X.A.,
630 Bellerby, R.G.J., Goyet, C., Metzl, N., Ríos, A.F., Pérez, F.F., 2009b. Anthropogenic
631 carbon distributions in the Atlantic Ocean: data-based estimates from the Arctic to the
632 Antarctic. *Biogeosciences* 6, 439-451

633 Winkler, L.W., 1888. Die Bestimmung des im Wasser gelösten Sauerstoffes. Berichte
634 der deutschen chemischen Gesellschaft 21, 2843-2854

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639

640 **Fig. 1** Map of the location of the Gulf of Cadiz and the Strait of Gibraltar and sampling
641 grid during the P₃A₂ cruise.

642

643 **Fig. 2** θ/S diagram of the study area from 100 dbar depth to the bottom: a) CTD data.
644 Red stars represent the water types (WT) for the different water bodies (NACW,
645 NADW and MOW) used for the eOMP analysis; b) A_T ($\mu\text{mol kg}^{-1}$); c) AOU ($\mu\text{mol kg}^{-1}$);
646 C_T ($\mu\text{mol kg}^{-1}$). Contour lines represent density anomaly expressed in kg m^{-3} .

647

648 **Fig. 3** Vertical distributions of a N-S transect from 100 dbar to the bottom: a) Map of
649 the selected stations; b) Salinity; c) Potential temperature ($^{\circ}\text{C}$), d) Total Alkalinity (A_T)
650 in $\mu\text{mol kg}^{-1}$, e) Total Inorganic Carbon (C_T) in $\mu\text{mol kg}^{-1}$ and e) Apparent Oxygen
651 Utilization (AOU) in $\mu\text{mol kg}^{-1}$.

652

653 **Fig. 4** Vertical distributions of an E-W transect from 100 dbar to the bottom: a) Map of
654 the selected stations; b) Salinity; c) Potential temperature ($^{\circ}\text{C}$), d) Total Alkalinity (A_T)
655 in $\mu\text{mol kg}^{-1}$, e) Total Inorganic Carbon (C_T) in $\mu\text{mol kg}^{-1}$ and e) Apparent Oxygen
656 Utilization (AOU) in $\mu\text{mol kg}^{-1}$.

657

658 **Fig. 5** Vertical distributions of a N-S transect from 100 dbar to the bottom: a-c)
659 Estimates of C_{ANT} ($\mu\text{mol kg}^{-1}$) from the ϕC_T° , ΔC^* and TrOCA₂₀₀₇ methods respectively;
660 d-f) percentage of NACW, NADW and MOW obtained by the eOMP analysis.

661

662 **Fig. 6** Vertical distributions of an E-W transect from 100 dbar to the bottom: a-c)
663 Estimates of C_{ANT} ($\mu\text{mol kg}^{-1}$) from the ϕC_T° , ΔC^* and TrOCA₂₀₀₇ methods respectively;
664 d-f) percentage of NACW, NADW and MOW obtained by the eOMP analysis.

665

666

Table 1. Biogeochemical characteristics of the water types selected as end-members in the eOMP analysis.

	NACW		NADW	MOW
	WT1	WT2	WT3	WT4
Θ ($^{\circ}\text{C}$)	17.3	11.3	2.4	13.1
S	36.50	35.55	34.93	38.50
O_2 ($\mu\text{mol kg}^{-1}$)	217	179	235	167
Si ($\mu\text{mol kg}^{-1}$)	0.1	7.7	22.8	9.9
NO_3 ($\mu\text{mol kg}^{-1}$)	2.05	15.56	20.55	10.81
PO_4 ($\mu\text{mol kg}^{-1}$)	0.16	1.14	1.39	1.20
A_T° ($\mu\text{mol kg}^{-1}$)	2362	2327	2300	2581
$\Delta\text{C}_{\text{dis}}$ ($\mu\text{mol kg}^{-1}$)	-17	-6	-8	0

Table 2. Specific C_{ANT} inventories in the area and the specific Mediterranean contribution (number of stations used=31, surface area=14,082 Km²).

Method	Specific Inventory (mol C m ⁻²)	Contribution of MOW to the specific inventory (%)
φC_T°	33.5±3.2	8
ΔC^*	34.2±3.2	8
TrOCA ₂₀₀₇	33.7±3.0	11
TrOCA ₂₀₀₄	38±3.1	12

Figure1
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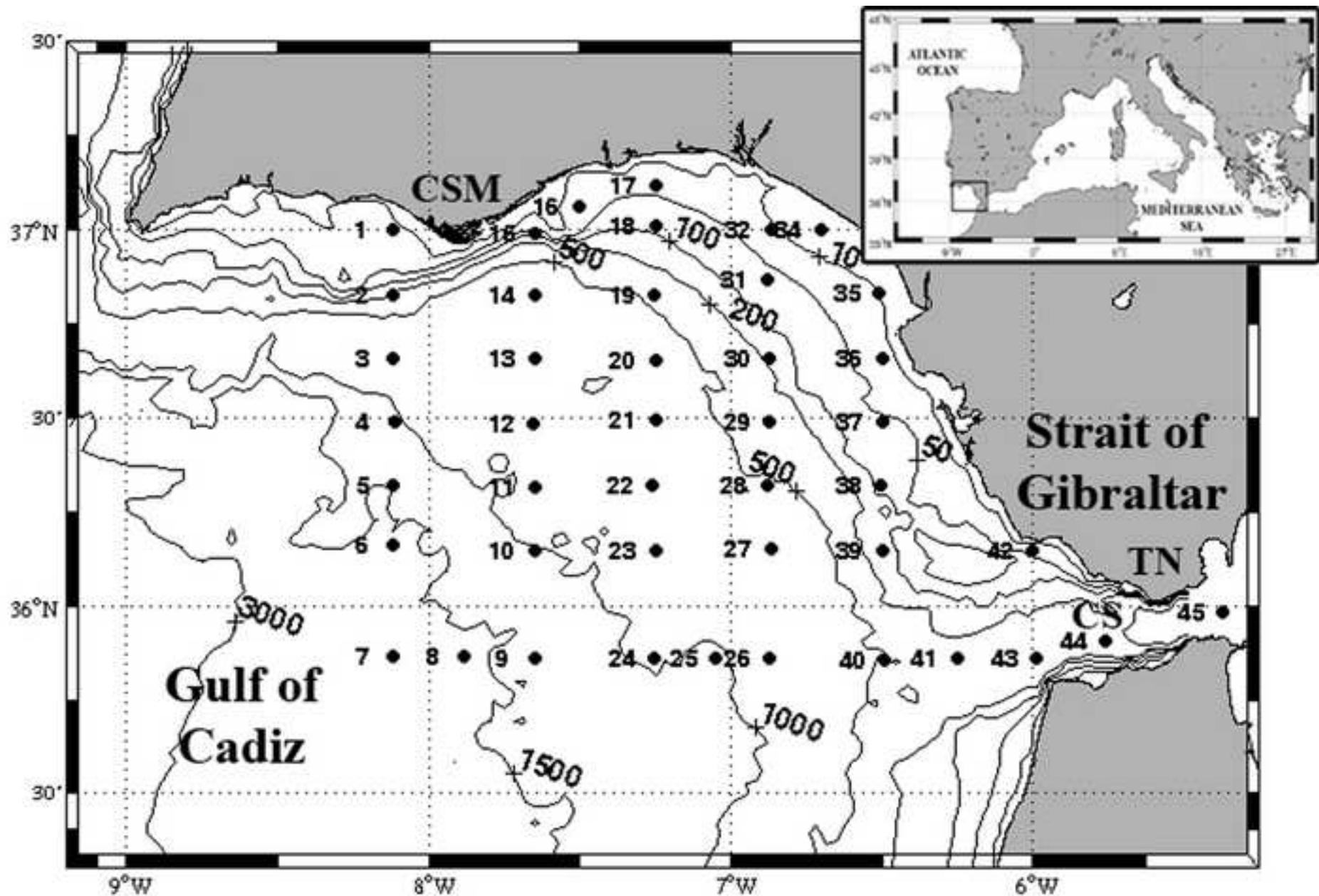


Figure2

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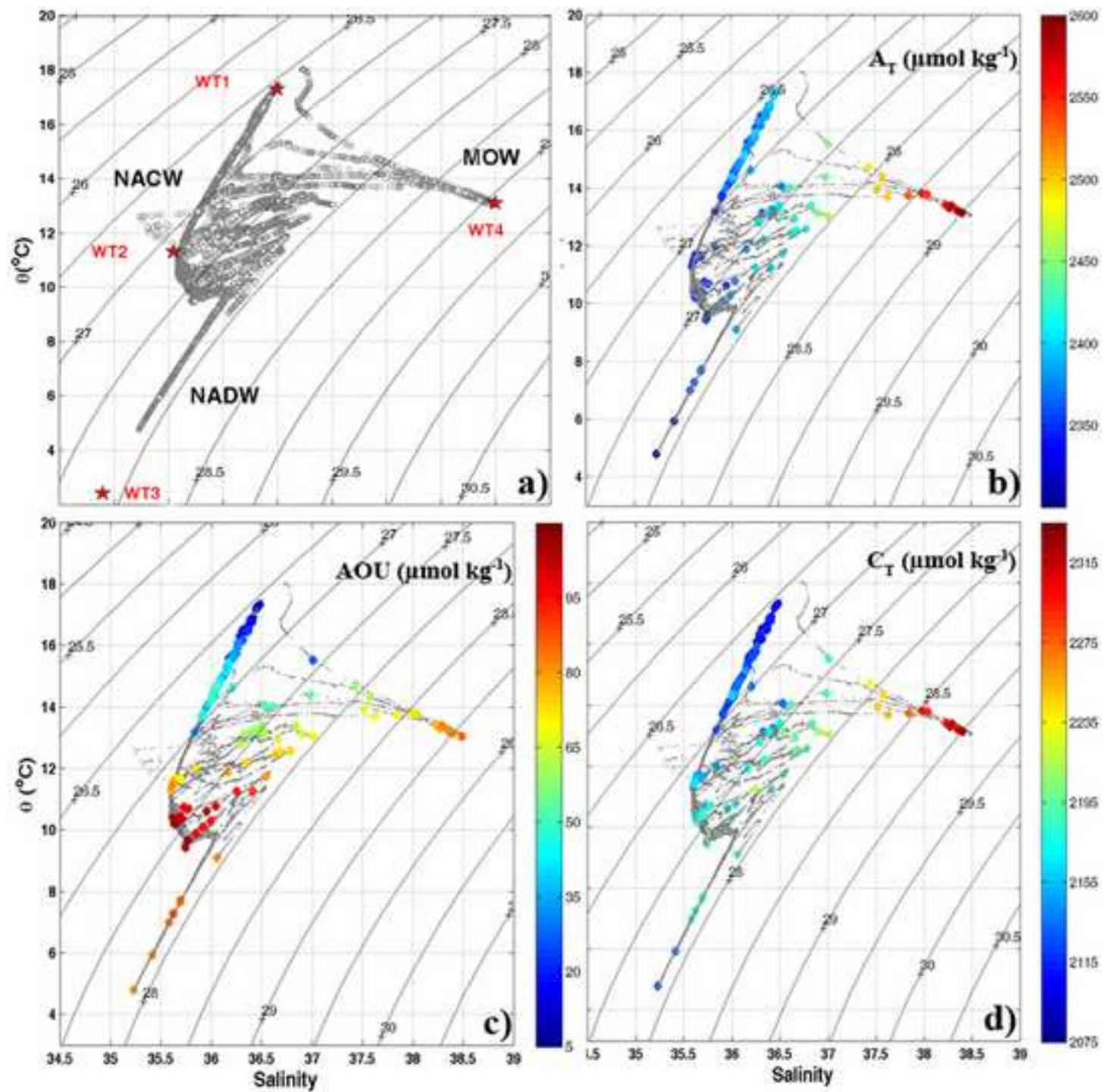


Figure3
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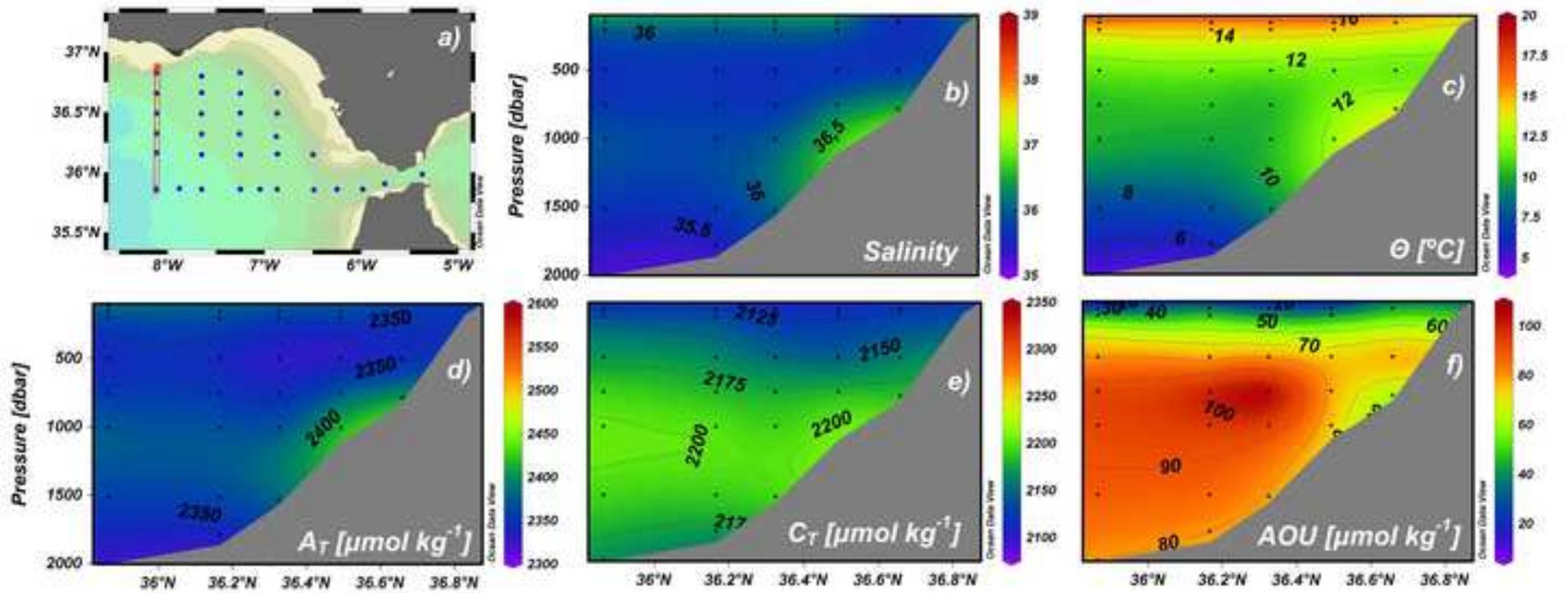


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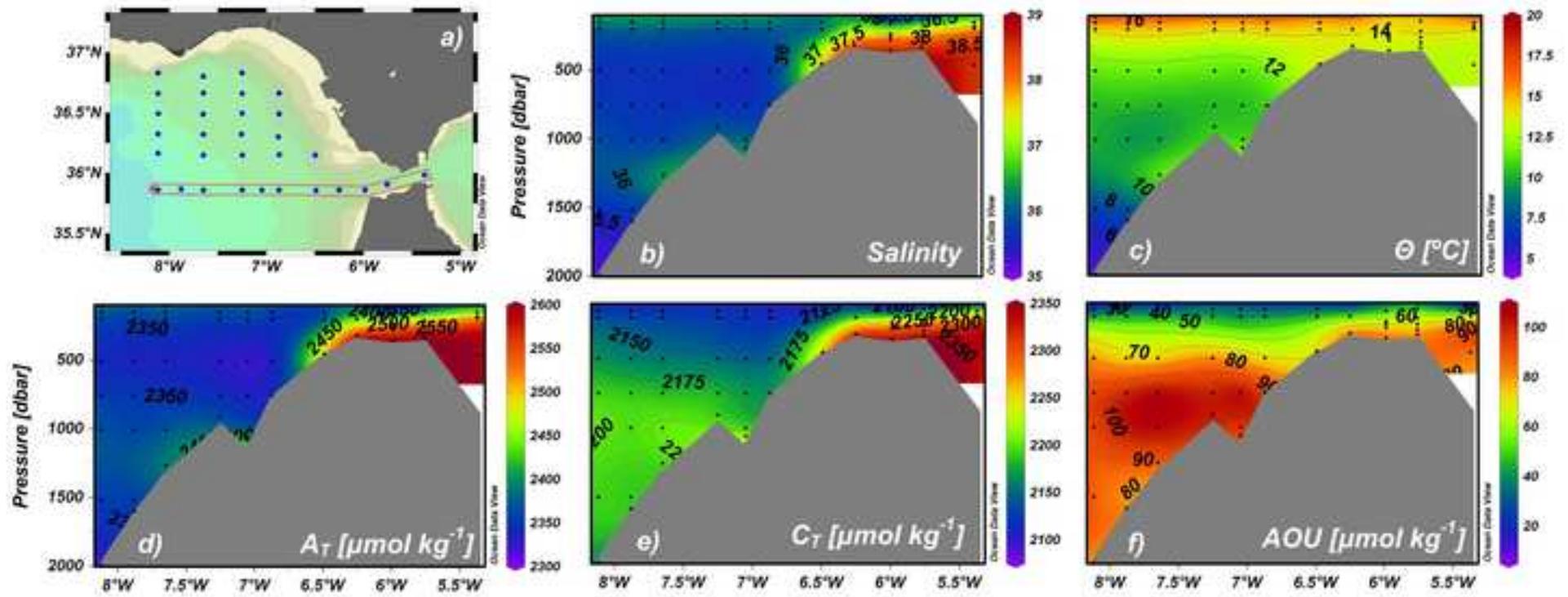


Figure5

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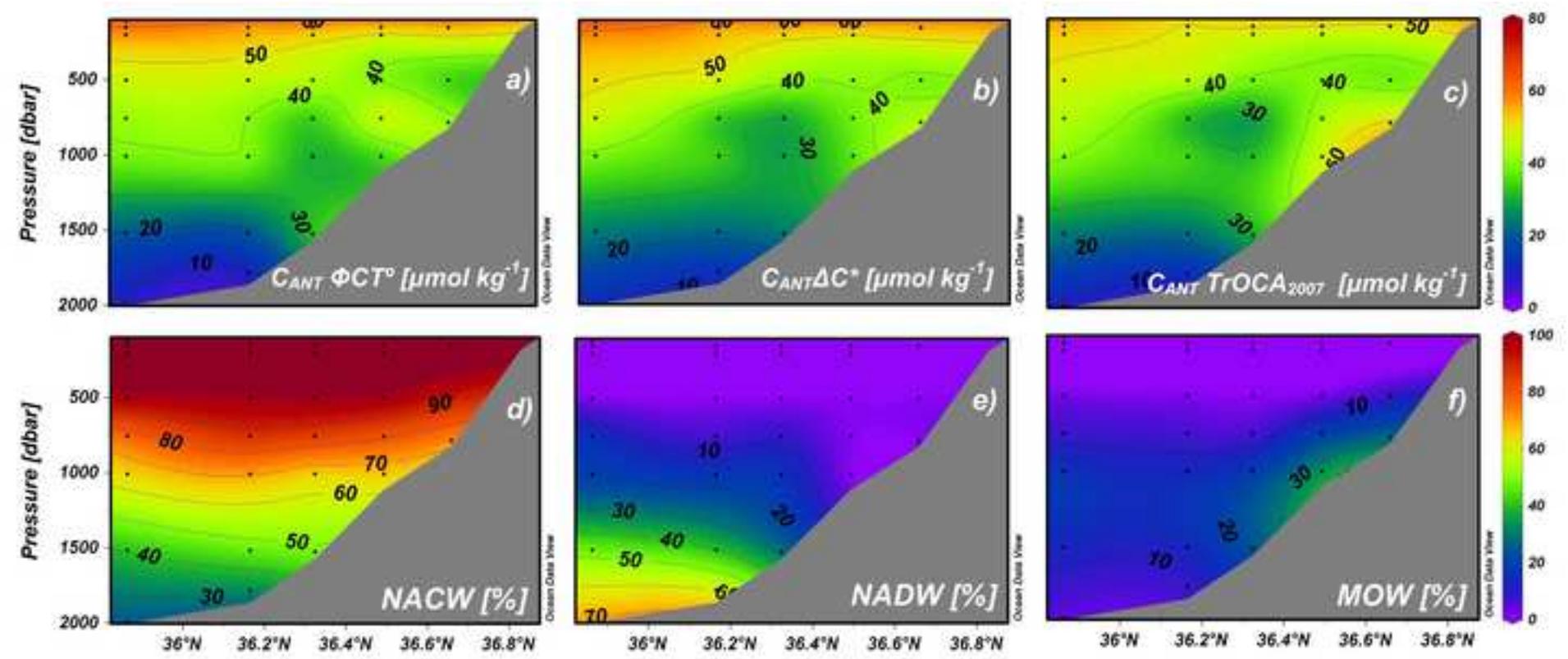


Figure6
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